POLYESTER SYNTHESIS USING HIGH PRESSURE CARBON MONOXIDE

By

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POLYESTER SYNTHESIS USING HIGH PRESSURE CARBON MONOXIDE

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Several transition metal complexes were investigated as potential catalysts for the copolymerization of epoxides with carbon monoxide. Cationic transition metal complexes displayed only the ability to open the epoxide ring without being able to incorporate carbon monoxide. These systems formed predominantly polyethers along with aldehyde and dioxane side products. Anionic transition metal complexes showed minimal reactivity with epoxides and produced no esters. The catalyst system of $Co(acac)_3$ and $AlEt_3$ effectively copolymerizes propylene oxide and carbon monoxide to make poly-β-hydroxybutyrate (PHB). The type of cobalt and aluminum compounds are very specific in this catalyst system. The neutral transition metal complex [(1,2,5,6-η)-1,5-cyclooctadiene][(1,2,3-η)-2-cycloocten-1-yl] cobalt, **10**, has also displayed the ability to catalyze the copolymerization of propylene oxide and carbon monoxide to create PHB. Other neutral cobalt complexes such as $CH_3C(X)CHC(X')CH_3CoC_8H_{12}$, X,X' = O(**11**), X,X' = NPh(**12**) also act as catalysts for this copolymerization, although they are much less active than **10**.

The structures of **11** and **12** along with a variety of others such as X = O, X' = NPh(**21**) and hydridotris(pyrazolyl)borateCoC_8H_{12}(**23**) have been characterized by NMR spectroscopy, and X-ray crystal structures of **12**, **21**, and **23** have been determined. Compounds such as **21** which have an unsymmetrical ligand display fluxional behavior in solution at room temperature due to isomerization of the enamido ketonate ligands. Lewis base (PMe_3, CO, and *t*-BuNC) adducts for **11** were observed and geometries for these compounds are discussed.

An alternative polymerization to make polyesters was developed. Copolymerization of ethylene glycol, propane diol, and butane diol with 1,9-decadiene and carbon monoxide led to a series of low molecular weight poly(alkylene dodecanedioates). Copolymerization of the unsaturated alcohol, ω-undecylenyl alcohol, with carbon monoxide led to low molecular weight poly(ω-undecylenoate). The molecular weights of these polymers can be increased by heating at 150 °C under vacuum for 24h.

CHAPTER 1
INTRODUCTION AND BACKGROUND

Polyethylene Terephthalate

Polymers have become ubiquitous in our everyday lives, from polyolefins in packaging to polyesters in clothing. The most widely produced polyester in the world is polyethylene terephthalate (PET). In the 1940's Carothers discovered that linear aliphatic polyesters displayed fiber properties. Today PET fibers are commonplace in clothing, carpets, and a variety of other fiber-containing products. Another large market for PET is in plastic bottles for the beverage industry.

PET is the polycondensation product of terephthalic acid with ethylene glycol. Terephthalic acid is produced from the oxidation of *p*-xylene while ethylene glycol is prepared from the hydration of ethylene oxide. Industrially, PET is prepared in a two stage process starting either from the transesterification reaction of dimethyl terephthalate with ethylene glycol or direct esterification reaction of terephthalic acid with ethylene glycol (**Figure 1.1**)(Ravindranath and Mashelkar 1986). For either reaction to form high polymer, the monomers must be in an exact 1:1 ratio. If the stoichiometry is not exact, only low molecular weight polymers will form. The initial step in the industrial production of PET occurs when an excess of ethylene glycol is allowed to react with either dimethyl terephthalate or terephthalic acid. This reaction forms a PET macromonomer, but more importantly it eliminates the stoichiometry problems associated with a two monomer system. The macromonomer is then heated under vacuum to eliminate ethylene glycol and form a high polymer.

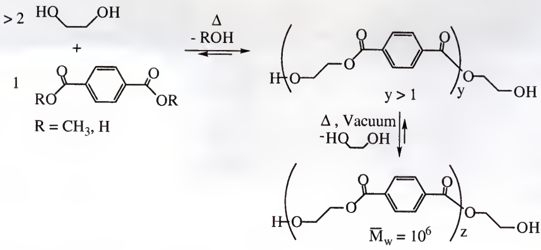


Figure 1.1 Industrial polyethylene terephthalate synthesis.

The polymerization of ethylene glycol with dimethyl terephthalate or terephthalic acid is classified as a step condensation mechanism. This is a condensation reaction, as opposed to an addition reaction, because with every reaction of a functional group, a byproduct is given off. Removal of the byproduct molecule, methanol or water for formation of the macromonomer and ethylene glycol for the reaction of the macromonomer to produce PET, drives the reaction toward polymer formation by eliminating any reverse reaction. In an addition polymerization, since no byproduct is given off, the polymerization must be driven entirely by the release of energy. Also, without the ability to remove a byproduct, there is no way to limit any reverse reaction which would depolymerize the growing polymer.

Polymerizations can also be divided into step growth and chain growth mechanisms. In a step polymerization, difunctional monomers first react with each other to produce dimers. These dimers eventually build up in concentration and then react with monomers or other dimers forming trimers and tetramers (Allcock 1990). Only at high conversions can high molecular weight polymers be produced (**Figure 1.2**). The extent of conversion is limited by catalyst activity and monomer purity. Monomers that are not perfectly difunctional can cap a growing polymer with an unreactive endgroup which limits the polymer molecular weight. In contrast to the step polymerization is the chain polymerization. In a chain polymerization, monomer is added to the active polymer chain end. This allows formation of high molecular weight polymers quickly and with only modest conversions. Normally in a chain polymerization, molecular weights are limited due to chain transfer and chain termination reactions which compete with the polymerization mechanism. Occasionally, a chain polymerization will occur where there are no transfer or termination reactions and this is termed a living reaction. In a living reaction, the polymer chains will continue to grow until all monomer has been consumed. Upon addition of more monomer or a different monomer, polymerization will continue.

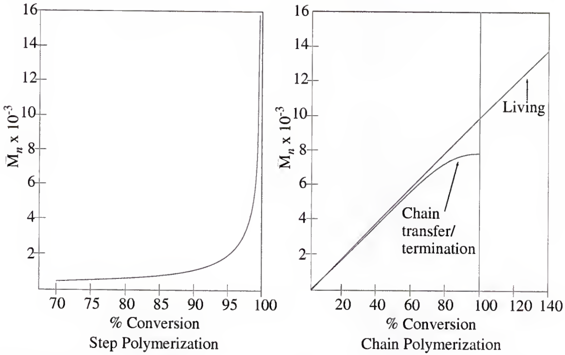


Figure 1.2 Molecular weight versus conversion for step and chain polymerizations.

As with most industrial processes, the use of catalysis is crucial for the production of PET. Lowering activation barriers in the process saves companies millions of dollars in energy costs. The catalysts used in PET production are specific to the stage of the reaction. For the transesterification reaction between dimethyl terephthalate and ethylene glycol, catalysts such as $Zn(OAc)_2$, $Mn(OAc)_2$, and $Ca(OAc)_2$ are employed. These catalysts maintain a high activity as long as the concentration of carboxylic acid is low (Walker 1983). Increased concentration of carboxylic acid severely poisons these catalysts. The mechanism for this catalysis is thought to proceed via a reaction of a metal complex with the alcohol to produce a metal alkoxide. The metal alkoxide then transfers its alcohol to the terephthalate ester creating a new ester. In the polycondensation reaction of the PET macromonomer, different catalysts are used. As the polycondensation proceeds, the concentration of hydroxyl endgroups decreases. SbO_3 and $Sb(OAc)_3$ have been used as catalysts, and although less active than the transesterification catalysts, their activities increase as the concentration of hydroxyl endgroups decrease. These systems are also stable in the presence of carboxylic acids which make them useful for the polycondensation of the PET macromonomer synthesized from terephthalic acid and ethylene glycol (Ravindranath and Mashelkar 1986). It is thought that these catalysts coordinate to the ester carbonyl, making the ester more electrophilic and prone to nucleophilic attack by an alcohol.

An alternate process for the production of PET involves the use of ethylene oxide instead of ethylene glycol (Mares 1969), eliminating the need to produce ethylene glycol from ethylene oxide in an earlier reaction. This process consists of the reaction of ethylene oxide directly with terephthalic acid to produce bis(hydroxyethyl)terephthalate (**Figure 1.3**). Unfortunately, the explosive nature of ethylene oxide makes this reaction a potential hazard to perform on a large scale.

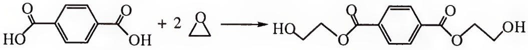


Figure 1.3 Reaction of terephthalic acid with ethylene oxide.

Poly-β-hydroxybutyrate

Another thermoplastic polyester that is gaining industrial significance is Poly-β-hydroxybutyrate or PHB. What makes PHB an attractive product is its biodegradability (Sanders 1994; Jedlinski 1997) and biological compatibility. PHB shows a slow degradation rate in the body making it a useful material for medical applications such as surgical sutures and drug delivery systems (Doi 1990). Currently PHB is made either by utilizing microorganisms or from the ring opening of butyrolactone (**Figure 1.4**).

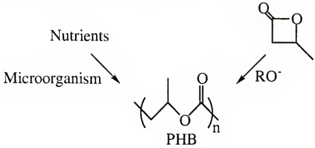
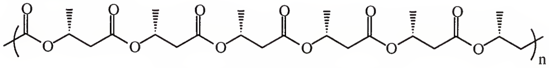
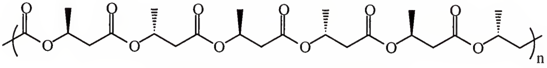


Figure 1.4 Syntheses of PHB.

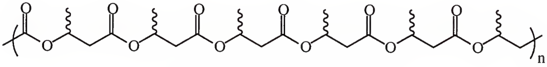
Isotactic PHB has a $T_g = 4$ °C and a $T_m = 180$ °C similar to that of isotactic polypropylene (Doi 1990), but unfortunately at a cost of $5/lb, PHB is much more expensive than polypropylene. Isotactic polypropylene is the most useful polypropylene, especially in the area of packaging (Horton 1994), an area where PHB's biodegradability would be an advantage. Tacticity of a polymer is a measure of stereoregularity in the polymer backbone. There are three types of tacticity: isotactic, syndiotactic, and atactic (**Figure 1.5**). An isotactic polymer contains pendant side chains with identical stereochemistries. The continuous repeat of stereochemistry leads to a highly crystalline polymer. A syndiotactic polymer contains pendant side chains with opposite stereochemistries. Again, as with isotactic polymers, this regular repeat of stereochemistry leads to a highly crystalline polymer. An atactic polymer contains a random mixture of stereochemistries for its pendant side chains. The random nature of the polymer does not allow good packing interactions between polymer chains and leads to a non-crystalline, waxy or oily polymer.



Isotactic Poly-β-hydroxybutyrate



Syndiotactic Poly-β-hydroxybutyrate



Atactic Poly-β-hydroxybutyrate

Figure 1.5 The three stereochemical structures of PHB.

The common method of making PHB is through the use of microorganisms. Many microorganisms produce PHB as carbon or energy reserves, often storing as much as 80% of their weight as PHB. The general metabolic pathway for PHB synthesis in *A. eutrophus* as well as other organisms has been determined (Doi 1990) (**Figure 1.6**). The pathway starts with a conversion of nutrients to acetyl-coenzyme A. Two molecules of acetyl-coenzyme A then condense to form acetoacetyl-coenzyme A, which is then reduced with NADPH to D(-)-3-hydroxybutyryl-coenzyme A. Finally polymerization is induced by poly(3-hydroxybutyrate) synthase. Because this reaction is performed in a biological system the resulting polymer is perfectly isotactic. Normally, biological systems synthesize a polymer whose repeat unit has an R absolute configuration. Various substrates can be used as nutrients in the biological synthesis of polyester. Addition of long chain alkanoic acids and alcohols as nutrients gives rise to copolymers of poly-β-hydroxybutyrate with other alkanoates. These copolymers have shown improved mechanical properties over pure PHB which tends to be fairly brittle. Industrially the copolymer polyhydroxybutyrate-*co*-hydroxyvalerate (P(HB-*co*-HV)) is produced and sold under the trade name Biopol™ (Holmes 1985).

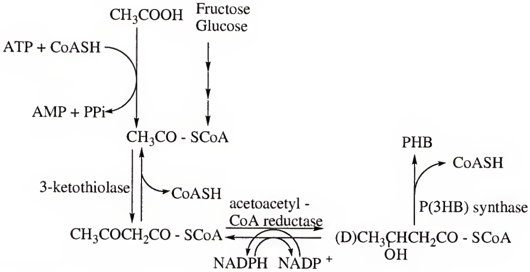


Figure 1.6 Pathway for biological conversion of nutrients to PHB (Doi, 1990).

PHB can be prepared through the polymerization of β-butyrolactone using a variety of initiators, including alkoxides (Jedlinski 1997) and aluminoxanes (Lenz 1998). Anionic polymerization of β-butyrolactone initiated using potassium methoxide/18-crown-6 proceeds by a living chain addition mechanism (Jedlinski 1991) (**Figure 1.7**). Potassium methoxide initiates the polymerization through an elimination reaction with β-butyrolactone forming potassium/crown methyl-2-oxybutyrate. This alkoxide eliminates potassium/crown hydroxide along with 2-methyl methacrylate. Potassium/crown hydroxide then nucleophilically ring-opens a molecule of β-butyrolactone forming a hydroxycarboxylate. The hydroxycarboxylate can react with β-butyrolactone starting the polymer propagation, or it can eliminate water forming a potassium/crown methacrylate. This potassium/crown methacrylate can also react with β-butyrolactone starting the polymer propagation. Propagation continues until monomer is completely consumed or the reaction is quenched. The living nature of this reaction allows addition of an second monomer to the living polymer creating block copolymers with various properties not available through microbial syntheses (Jedlinski 1997). Polymers produced using alkoxide initiators with a racemic mixture of β-butyrolactone tend to be atactic, although the use of aluminoxane initiators creates polymers with blocks of R and S stereoisomers (Lenz 1995, 1998).

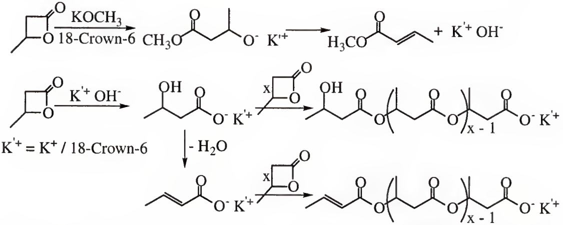


Figure 1.7 Anionic polymerization of β-butyrolactone with potassium methoxide/18-Crown-6.

The attractiveness of PHB, along with its physical properties, is its environmental degradability. This biodegradability has been shown to take place in a variety of environments including soil, sludge and sea water (Doi 1990). The mechanism for degradation in sea water appears to be through hydrolysis of the esters. Although not a degradation through biological methods, sea water degradation is still considered biodegradation. Both PHB and P(HB-co-9%Hv) films have shown complete decomposition in 20 °C sea water over 8 weeks. However, the non sea water biodegradability of these polymers has been shown to be dependent on the tacticity of the polymer. Since bacteria produce PHB's as energy storage, these same bacteria have the ability to degrade the polymers. However, while the bacteria can degrade the highly isotactic PHB that they produce, the same bacteria cannot normally degrade pure atactic PHB produced through β-butyrolactone polymerizations (Jedlinski 1997; Gross 1992). Biodegradability can be induced in atactic PHB if it is blended with isotactic PHB.

Transition Metal Catalyzed Polyesterifications

Although there are no industrial polyesterifications which rely solely on transition metal catalysis, there are a few examples of polyesterifications which do require a transition metal catalyst. The use of transition metals allows for the development of polymers not attainable through normal organic reaction chemistry. Perri (1990; 1992) and Sugi (1996) have developed the reaction of para-disubstituted benzenes with diols and carbon monoxide to form poly alkylene terephthalates (**Figure 1.8**). Perri's reaction employs a palladium system which switches between Pd(II) and Pd(0) and it is observed that the nature of the catalyst precursor is not of major importance. A variety of precursors have been employed, both Pd(0) and Pd(II) along with a variety of ligand environments and the reactivity of each is similar. Every precatalyst used appears to form the same or similar active catalytic species in solution. The mechanism for polymerization starts when a phenyl halide oxidatively adds to palladium to make a palladium-aryl complex. Carbon monoxide then inserts into the palladium-aryl bond forming a palladium-acyl complex. Finally, alcohol reacts with the metal complex, eliminating an ester along with one equivalent of the acid HY. The reaction can be driven by adding a base such as pyridine to remove HY from the system. Even with removal of HY, the polymer is reported to be only of moderate molecular weights. Sugi has improved on this reaction by using 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) as a base and bisdiphenylphosphino propane as a ligand for palladium. These changes to Perri's system gives polymers with molecular weights on the order of 10^6.

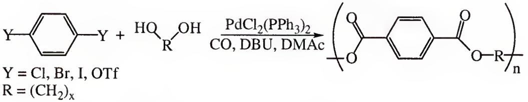


Figure 1.8 Palladium catalyzed polymerization of paradisubstituted benzene, diol and carbon monoxide.

Inoue (1996) has developed a method for incorporating carbon dioxide into a catalytic system to make polyesters. In this system diynes are allowed to react with alkyl dihalides under an atmosphere of carbon dioxide forming poly(alkyl alkynoates). The proposed mechanism starts with reaction of the terminal alkyne with copper halide (**Figure 1.9**). Potassium carbonate scavenges HX and a copper acetylide is formed. Potassium carbonate is used instead of organic bases such as triethylamine since amines are easily alkylated by alkyl halides. Nucleophilic attack by the acetylide on carbon dioxide forms a copper carboxylate complex. Reaction of the copper carboxylate with alkyl halide produces an ester and reforms the copper halide. Molecular weights of these polymers vary, with the highest reported as $M_n = 6000$. Primary aliphatic dibromides produce higher polymers than either secondary aliphatic dibromides or primary aliphatic diiodides. Addition of 1,10-phenanthroline, which chelates to copper, accelerates the reaction with no increase in yields or molecular weights.

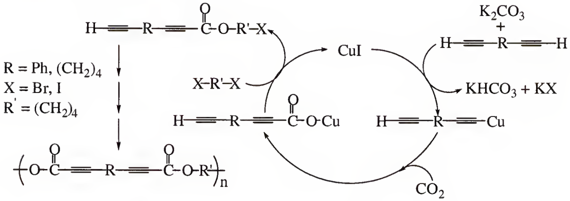


Figure 1.9 Proposed mechanism for formation of polyesters from terminal diynes, aliphatic dihalides and carbon monoxide.

Metal Catalyzed Homopolymerization of Epoxides

When looking for a monomer to polymerize, thermodynamics must be taken into consideration. Monomers which are high in energy can release this energy during the polymerization to favor products. Epoxides provide an excellent monomer for polymerizations. A substantial amount of ring-strain energy exists in this cyclic ether and can be released during a ring-opening reaction. Several catalytic systems have been developed to polymerize epoxides to make polyethers and most of these utilize the Lewis acidity of a transition metal to assist in the ring opening of the epoxide.

In 1955, Pruitt discovered that the reaction of $FeCl_3$ with racemic propylene oxide (PO) produced a surprisingly stereoregular polypropylene oxide. Lenz (1997) has studied the reaction of racemic propylene oxide with a variety of catalysts. $FeCl_3 \cdot PO$, $Al(iBu)_3/H_2O$, and $AlEt_3/H_2O$ all show ability to produce polymers with a modest degree of stereoregularity. Typically, these polymers contain only 60-70% isotactic diads. Another catalyst can be made from the reaction of isobutylalumoxane (IBAO) with two equivalents of propylene oxide at low temperatures. This new species, the adduct IBAO·PO, will polymerize racemic propylene oxide into highly crystalline polypropylene oxide up to a $M_w = 10^5$. Wu (1990) has developed a system of $Nd(acac)_3$ (acac = acetylacetone) with six equivalents of $AlEt_3 \cdot 1/2\ H_2O$ as a catalyst. When mixed with propylene oxide this system also produces crystalline polyether with $M_w = 10^6$. Shen (1989) has developed a catalyst system using ytterbium. Reacting ethylene oxide with a mixture of $Y(P_{204})_3$ ($P_{204} = ((CH_3CH_2)_2CHCH_2O)_2P(O)OH$) with six equivalents of $Al(iBu)_3 \cdot H_2O$, polyethylene oxide with $M_w = 10^6$ is formed.

It has been proposed that the polymerization of epoxides using these catalyst systems requires multiple metal sites (Vandenberg 1964). The purpose of these sites is for one metal to be attached to the polymer chain while the other metal acts as a Lewis acid to coordinate the monomer and facilitate the ring opening reaction. The polymers formed have a wide variety of uses depending on molecular weight. Low to medium molecular weight polyoxyethylene glycols have uses in pharmaceutical applications, as plasticizers and lubricants. High molecular weight polyoxyethylene glycols have uses as water soluble films, coagulants, and foam stabilizers (Sandler 1974).

Copolymerization of Epoxides with Carbon Dioxide

Epoxides can be copolymerized with a variety of substrates to create functional groups not easily accessible through homopolymerization. One of the most common comonomers is carbon dioxide. The resultant polymer is a linear polycarbonate with a two-carbon alkyl chain between each carbonate functionality. The creation of polycarbonates using carbon dioxide and epoxides is of importance both because of the inexpensiveness of the reactants and the wide array of epoxides available to make polymers with a wide variety of properties. Industrially polycarbonates are made from the condensation of terminal diols with phosgene, a highly toxic compound (Sandler 1974).

Inoue (1969a,b) first described the reaction of a series of metal complexes with epoxides and carbon dioxide to form polycarbonates(**Figure 1.10**). While a mixture of $ZnEt_2$ and water catalyzes the formation of both polycarbonate and cyclic carbonate, $ZnEt_2$ alone shows no catalytic activity. Butyllithium alone shows only low activity for the polymerization. Under an atmosphere of carbon dioxide, $ZnEt_2/H_2O$ catalyzes the formation of a polymer with 88% carbonate repeat units and 12% ether repeat units Increasing the pressure to 50 atm produces only carbonate repeat units in the polymer with M_w = 50000 - 150000. This polymer shows a perfect head to tail structure which means there is a distinct preference for the regiochemistry for opening the epoxide (Inoue 1976). This polymer is amorphous with a glass transition temperature of 30 °C. Upon heating to 180 °C the polymer can be completely depolymerized to cyclic carbonate. Substitution of epoxide with other cyclic ethers such as oxetane or tetrahydrofuran shows no conversion to polymer using the $ZnEt_2/H_2O$ catalyst .

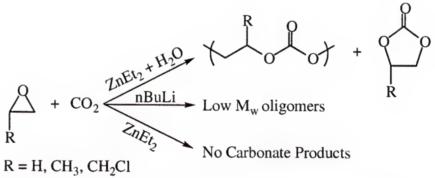


Figure 1.10 Reaction of epoxides with carbon dioxide using different catalysts.

Adjustment of the ligand environment around the metal can greatly enhance the activity and lifetime of the catalyst. Darensbourg (1995) has shown that by using (2,6-diphenylphenoxide)$_2$Zn(ether)$_2$ high conversions of cyclohexene oxide with carbon dioxide can be accomplished. The use of bulky ligands forces the metal to remain monomeric, whereas the catalytic system of $ZnEt_2/H_2O$ contains a mixture of multimetallic species. The catalyst's activity is very high at 366 g polymer / g catalyst compared to the 5 g polymer / g catalyst seen in earlier systems (Beckman 1997). Darensbourg's system creates copolymers of cyclohexene oxide and carbon dioxide which reach molecular weights of 200000, although polydispersities are broad. The temperature and pressure used are comparable to those used by Inoue (1969a,b). Interestingly, using propylene oxide instead of cyclohexene oxide produces predominately cyclic carbonate.

Beckman and coworkers (1997) created a catalyst from the reaction of zinc oxide with the condensation product of tridecafluorooctanol with maleic anhydride. Although the exact structure of the catalyst is not known, the system is highly reactive toward the copolymerization of cyclohexene oxide with carbon dioxide. The catalyst is very soluble in carbon dioxide, so much that the reactions are run using supercritical carbon dioxide as a solvent, which eliminates the need for an organic solvent. The catalyst is similar in activity to Darensbourg's with measured activities as high as 400 g polymer / g catalyst. The molecular weights of the polymers produced under various conditions range from 50000 to 180000 with the highest molecular weights achieved at 110 °C and 2000 psi.

Recently Inoue (1986) and Coates (1998) have developed living polycarbonate polymerization systems. Coates makes polycarbonates using a zinc catalyst containing a bulky β-diiminate ligand (**Figure 1.11**). The catalyst exists both as a monomeric species (**1**) and a dimer (**1a**) in solution as evidenced by the presence of two sets of peaks in the ^{1}H NMR spectrum, one of which increases while the other decreases as the concentration is decreased. While this catalyst shows almost no activity for the homopolymerization of cyclohexene oxide, in the presence of low pressures of carbon dioxide (100 psi) at moderate temperatures (20-80 °C), formation of polycarbonate rapidly occurs. The stereochemistry of the cyclohexane rings in the polycarbonate is exclusively *trans* and the repeat unit is predominately carbonate, although a small amount of ether linkage may exist. The polymer reaches molecular weights on the order of 30000 with polydispersities between 1.1 and 1.2, lending evidence to a living mechanism.

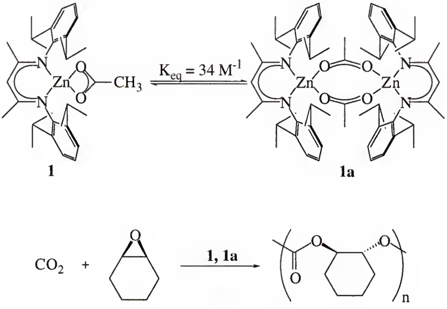


Figure 1.11 Zinc catalyst for cyclohexene oxide / carbon monoxide copolymer.

Inoue uses a catalyst system comprising of (TPP)AlCl (TPP = tetraphenylporphyrin) with Et_4NBr. Using this system, propylene oxide can be copolymerized with carbon dioxide to produce polycarbonates with polydispersities of 1.09 (**Figure 1.12**). The narrow polydispersity indicates a controlled chain polymerization mechanism, and the reaction is claimed to be living. This reaction proceeds through a catalyst which has two polymer chains growing from opposite sides of the aluminum.

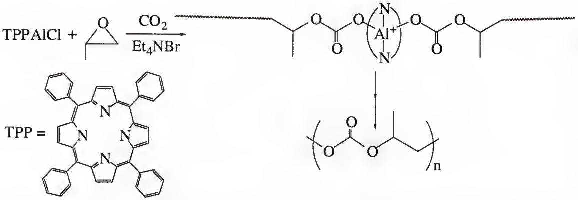


Figure 1.12 Living polycarbonate system with polymer growing from two sides of the catalyst.

The mechanism of polymer propagation appears to be the same regardless of catalyst although only with a well defined catalyst is the mechanism of polymer initiation also understood (Darensbourg 1998) (**Figure 1.13**). The reaction is initiated by attack of the ligand, usually halide or carboxylate, on a molecule of epoxide to form a metal alkoxide. If the catalyst contains an alkoxide, the alkoxide reacts with carbon dioxide to form a metal carbonate which reacts with a molecule of epoxide to form a metal alkoxide. The alkoxide which is formed nucleophilically attacks carbon dioxide to form a carboxylate. The polymerization is then propagated through nucleophilic attack on an epoxide by the carboxylate.

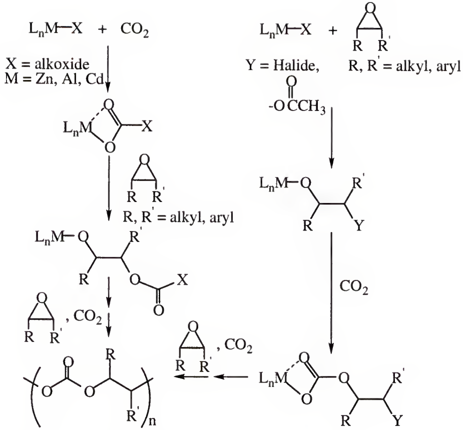


Figure 1.13 Mechanism for copolymerization of epoxides with carbon dioxide.

Copolymerization of Carbon Monoxide with Olefins

Another inexpensive gas that can be utilized through the use of transition metals in polymerizations is carbon monoxide. Reppe (1951) discovered that $K_2Ni(CN)_4$ could catalyze the copolymerization of ethylene and carbon monoxide in water to produce low molecular weight oligomers (**Figure 1.14**). The oligomer was shown to contain one ethylene molecule and one carbon monoxide molecule in the repeat unit arranged in a perfectly alternating manner. Previous work using radical initiators produced only random copolymers with a variable amount of CO incorporation which was always less than 50 mol % (Garbassi 1994). Shryne (1976) later showed that addition of triflic acid or *p*-toluene sulfonic acid gives much higher molecular weight polymers, although in low yields.

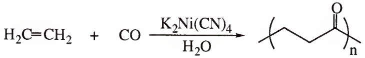


Figure 1.14 Copolymerization of ethylene with carbon monoxide.

Attempts to use either cobalt or rhodium as catalysts for this reaction gave only low molecular weight oligomers (Sen 1985). Switching catalysts from nickel to palladium can also produce polyketones. Using a catalyst system of bis(tertiaryphosphine)palladium dichloride, ethylene can be copolymerized with carbon monoxide producing polyketone at a high rate. Unfortunately, this reaction requires the use of very high temperature and pressure (250 °C and 1000 atm) (Drent, 1996). The ligand environment is very important for this reaction. Reacting ethylene with carbon monoxide in methanol using a catalyst system of palladium acetate with *p*-toluene sulfonic acid and excess tertiary phosphine yields exclusively methyl propionate. Changing to a catalyst system of palladium acetate with tosyl acid and one equivalent of 1,3-bis(diphenylphosphino)propane (DPPP) leads to high molecular weight polyketone (**Figure 1.15**) (Drent 1991).

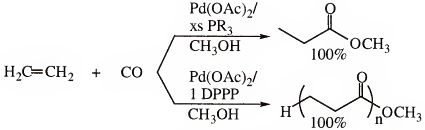


Figure 1.15 Effect of phosphine on product selectivity.

The rationalization for this selectivity is that with the bidentate phosphine, a *cis* coordination site is available. After formation of a metal-acyl, coordination of ethylene *cis* to the acyl is facilitated, allowing migratory insertion to occur. In the catalytic system employing excess tertiary phosphine, a *cis* insertion site is not available. Phosphines prefer to coordinate trans to each other forcing any open coordination site to be trans to a metal-acyl, which would not allow migratory insertion (Collman 1987). Alcoholysis of the metal-acyl then becomes the predominant reaction. Other bidentate ligands have been studied in this reaction, with the order of polymer molecular weights being diphenylphosphino propane > ethane > butane > pentane. In fact, diphenylphosphino pentane only gives low molecular weight oligomers. The resulting polymers formed are perfectly alternating between carbonyl and ethylene in the backbone, meaning that no multiple insertions of either carbon monoxide or ethylene occur. Insertion of carbon monoxide into metal-alkyl bonds is facile, energetically favored, and rapid, but insertion of carbon monoxide into a metal-acyl bond is disfavored. Olefin insertion into metal-acyl bonds also is facile, and while olefin insertion into a metal-alkyl bond is known, in this system that insertion is much slower than carbon monoxide insertion into a metal-alkyl bond.

Brookhart has studied the mechanism of the copolymerization of carbon monoxide with *t*-butyl styrene using a well-defined cationic palladium catalyst (**Figure 1.16**) (Brookhart 1992). The initial catalyst is a cationic palladium alkyl with a bidentate diimine ligand and a weakly coordinating counterion. Carbon monoxide displaces coordinated solvent, then inserts into the metal alkyl bond. Olefin then coordinates to the metal followed by insertion into the metal-acyl bond reforming a metal alkyl species.

Waymouth (1996) has studied an adaptation of the carbon monoxide / olefin copolymerization using a diene as the olefin. Hexadiene has been shown to react with carbon monoxide using a catalyst system of palladium acetate, DPPP, and 1,4-naphthaquinone in methanol to form a copolymer containing cyclic and linear ketone repeat units (**Figure 1.17**). The polymer is formed in low yield and low molecular weight.

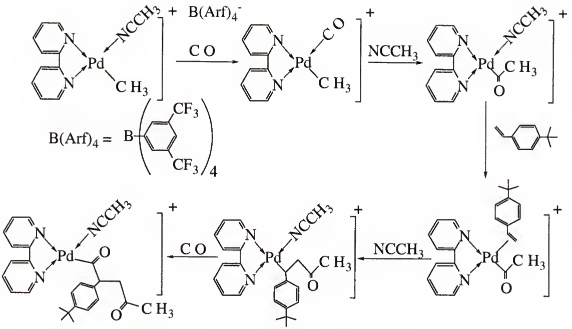


Figure 1.16 Mechanism for copolymerization of olefins with carbon monoxide.

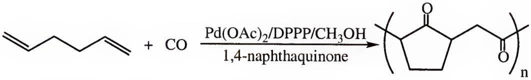


Figure 1.17 Polymerization of 1,5-hexadiene with carbon monoxide.

Switching solvent and ligand show a dramatic effect in the product formed. Changing the solvent to 95% chloroform and 5% methanol in this system increases the yield from 4% to 42% and increases the molecular weight from 5500 to 85000 and also changes the regioselectivity of the polymerization. The resulting polymer contains both five and six membered rings in the repeat unit. Changing the ligand from DPPP to 1,3-bis(diisopropylphosphino)propane (DiPP) changes the selectivity of the reaction to produce a polymer with only six membered rings in the backbone (**Figure 1.18**).

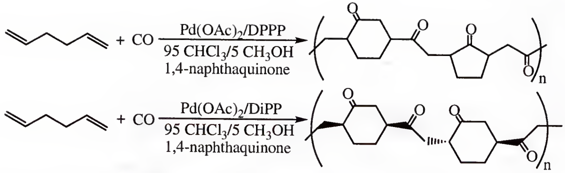


Figure 1.18 Polyketones formed using chloroform/methanol system.

Currently, there are no polyketones being marketed, but in 1993 Shell announced plans to build a 10000-15000 ton / year plant to produce aliphatic polyketones. Aliphatic polyketones with <5 mol % CO incorporation show physical properties identical to low density polyethylene, but they also show degradation when exposed to ultraviolet radiation (Garbassi, 1994). The melting temperature rises as the amount of CO incorporation in the polymer increases. At 50 mol % CO the T_m = 260 °C versus T_m = 110 °C for a polymer containing 10 mol % CO. The mechanical properties of the perfectly alternating polyketones show their strength to be intermediate between polypropylene and polyamides making them useful for high strength applications. Gas permeability data show that these polyketones possess similar attributes to PET, making them potentially useful as drink packaging. Finally, the carbonyl functionality in the polymer backbone allows for modification to obtain new functional polymers. Several functional groups including alcohols, amines and cyanohydrins have been synthesized from random CO / olefin copolymers, unfortunately modification of perfectly alternating copolymers has not been accomplished to date (Sen 1986).

This dissertation presents an investigation into two new transition metal catalyzed polymerizations to produce polyesters. The introduction has outlined several polymerization processes which have played major roles in the design of catalysts. The application of some of these catalysts along with other known transition metal systems toward the copolymerization of carbon monoxide with epoxides is covered in Chapter 2. This chemistry leads to the development of new transition metal complexes which are studied further in Chapter 4. The copolymerization of dienes with diols and carbon monoxide along with the copolymerization of $\alpha-\omega$ unsaturated alcohols with carbon monoxide is outlined in Chapter 3.

CHAPTER 2
DESIGN OF CATALYSTS FOR THE COPOLYMERIZATION OF EPOXIDES WITH CARBON MONOXIDE

Precedent for Polymerization of Epoxides with Carbon Monoxide

The idea of copolymerizing epoxides with carbon monoxide is relatively new, and its novelty limits the amount of precedent for this reaction. Therefore, any reference to the reaction of a transition metal with carbon monoxide and an epoxide was considered for insight into this reaction. Particularly of interest were reactions where an epoxide was carbonylated with carbon monoxide forming an ester functionality. Only a few citations for the carbonylation of epoxides give information as to what kind of catalyst would be effective in polymerizing epoxides with carbon monoxide.

Heck (1963) described the reaction of hydridocobaltcarbonyl and cobalt carbonyl anion with carbon monoxide and ethylene oxide or propylene oxide. At low temperatures, hydridocobaltcarbonyl reacts with carbon monoxide and an epoxide to form a hydroxyacyl cobalt species (**Figure 2.1**). Evidence suggests that this reaction proceeds initially through dissociation of the acidic proton on the cobalt and nucleophilic attack by the cobalt carbonyl anion on the epoxide forming, after protonation, an intermediate hydroxyalkyl cobalt species. This is followed by insertion of carbon monoxide into the metal-alkyl bond to form the hydroxyacyl species.

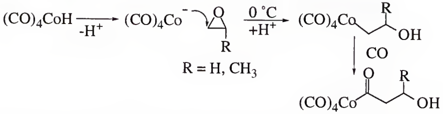


Figure 2.1 Reaction of hydridocobalt tetracarbonyl with carbon monoxide and epoxides.

When cobalt carbonyl anion is allowed to react with epoxides and carbon monoxide in the presence of an alcohol, a β-hydroxyester is formed (**Figure 2.2**). Again a hydroxyacyl species is thought to form which is then nucleophilically attacked by the alcohol forming the hydroxyester and regenerating cobalt carbonyl anion. The hydroxyester is produced in less than 30% overall yield.

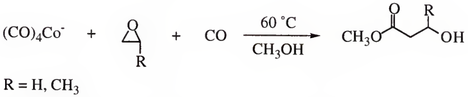


Figure 2.2 Reaction of cobalt tetracarbonyl anion with carbon monoxide and epoxides to produce β-hydroxyesters.

Drent and Krajtwijk (1994) described the carbonylation of epoxides to form lactones. A mixture of cobalt octacarbonyl and 3-hydroxypyridine gives 100% conversion of epoxide and 98% selectivity to the lactone (**Figure 2.3**). If left in the reaction mixture while exposed to air this lactone can homopolymerize to form a low molecular weight polyhydroxybutyrate.

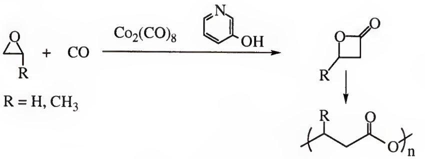


Figure 2.3 Reaction of epoxides with carbon monoxide to form lactones.

Drent's reaction does not seem as straight forward mechanistically as the Heck catalyst system. In Heck's case the catalyst acts as a nucleophile to open the epoxide ring, but in Drent's system it is not clear if the catalyst acts as a nucleophile toward the epoxide or simply oxidatively adds the epoxide. In polar solvents such as tetrahydrofuran, cobalt octacarbonyl is known to disproportionate into an anionic and cationic species (Edgell 1970). In Drent's system, propylene oxide is both substrate and, being an ether, a very polar solvent which could create a species similar to Heck's (**Figure 2.4**). The addition of hydroxypyridine may play a role similar to THF and form an adduct with cobalt stabilizing the heterolysis reaction.

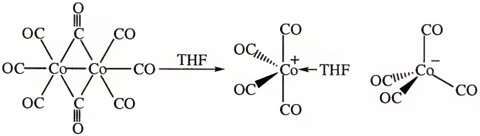


Figure 2.4 Disproportion of cobalt octacarbonyl in the presence of THF.

Testing Transition Metal Complexes as Potential Catalysts for the Copolymerization of Carbon Monoxide With Epoxides

Since there exists only limited precedent, development of a catalyst for the copolymerization of epoxides with carbon monoxide required that a broad approach be taken in the search. Several reaction schemes were postulated, taking into account known epoxide and carbon monoxide chemistry. Transition metal complexes were then synthesized which possessed characteristics necessary for these schemes. The three types of schemes that were developed and tested employed cationic, anionic, and neutral transition metal complexes, respectively. The following outline attempts to use these transition metal complexes as catalysts in the copolymerization of carbon monoxide and epoxides.

Attempt to use Cationic Late Transition Metals as Catalysts

It has been known for some time that acids ring-open epoxides. In organic syntheses Brønsted acids are commonly used to open an epoxide ring (Carey and Sundberg 1990). For this reaction the proton coordinates to the oxygen of the epoxide followed by a nucleophilic opening of the ring to form an alcohol (**Figure 2.5**).

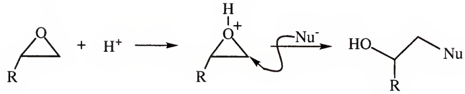


Figure 2.5 Ring-opening of epoxides by acids.

This reaction mechanism could be adapted to use a transition metal as a catalyst for opening the epoxide ring. An unsaturated cationic metal could possess both the Lewis acidity and coordinative ability to open the epoxide ring. An alkyl or acyl substituent must be covalently bound to this metal to become the growing polymer chain. The potential reaction would be insertion of carbon monoxide into the metal-alkyl bond and coordination of the epoxide to the metal. This would be followed by ring-opening of the epoxide and insertion of the oxygen into the acyl group, **1**, forming an ester linkage (**Figure 2.6**). The success of this scheme hinges on the third step of the process. While coordination and ring-opening of the epoxide should be facile, inducing the reaction of the oxygen with the metal acyl bond may not be as favorable.

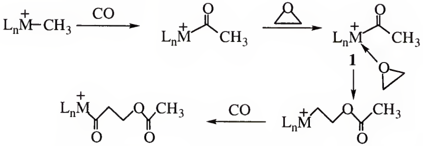


Figure 2.6 Proposed reaction scheme for polymerization with cationic transition metals.

A series of cationic palladium alkyl complexes based on Brookhart's polyketone catalyst (Brookhart 1992), bipyPd(NCMe)MeBAr$_4$ (bipy = 2,2' bipyridine, BAr = tetra(3,5-bistrifluoromethylphenyl) borate), were synthesized to test their activities as potential catalysts for polyester synthesis (**Figure 2.7**). Brookhart's catalyst was chosen because it is a cationic metal with an alkyl substituent, and has been shown to be an active catalyst for other polymerizations with carbon monoxide as mentioned in Chapter 1. Cationic palladium alkyl systems undergo a facile insertion of CO into the metal-alkyl bond forming an acyl complex. It was hoped that the cationic palladium metal center would be acidic enough to ring open the epoxide which would then insert into the palladium-acyl bond.

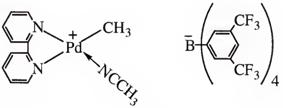


Figure 2.7 Cationic palladium complex tested as potential catalysts.

For these studies both propylene oxide and styrene oxide were used along with various pressures of carbon monoxide. Under conditions where the epoxide was diluted in solvent, no reaction was observed and unreacted epoxide was recovered. Under conditions where neat epoxide was used, an amorphous precipitate was formed upon addition of the reaction mixture to methanol. The IR spectra of the precipitates failed to show any absorptions in the carbonyl region (1650-1800 cm^{-1}) which would be expected for an ester product. The ^{1}H NMR spectra of the products were consistent with the formation of the polyethers, polystyrene oxide and polypropylene oxide, with resonances where ether protons are usually observed (δ 3-4 ppm). From these observations, it appeared that the metal was acting only as a Lewis acid for the polymerization of epoxides into polyethers (**Figure 2.8**). In this instance it seems that the opening of the epoxide ring is much faster than an insertion of the oxygen into palladium-acyl bond as in **1**, the crucial ester-forming step. The ring opening of the epoxide is enhanced by nucleophilic attack by an additional epoxide.

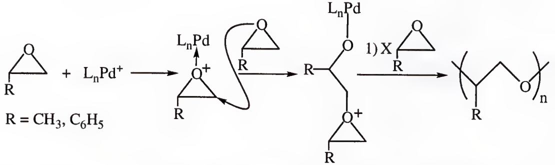


Figure 2.8 Homopolymerization of epoxides by cationic palladium complexes.

These reactions were repeated under high pressure and temperature using epoxide dissolved in solvent. In the case of styrene oxide, upon addition of the reaction solution to methanol a white precipitate formed which was determined by mass spectrometry and ^1H NMR spectroscopy to be an isomer of diphenyldioxane, most likely 2,5-diphenyldioxane. Dioxane has been observed as a byproduct in the polymerization of epoxides due to backbiting of the growing polymer chain onto itself (Allcock 1990).

Since the Brookhart system was seen to only ring-open the epoxides without insertion, modifications to the metal complexes were made to see if the insertion of the epoxide into the metal-acyl bond could be induced. Three other palladium complexes were synthesized with different ligand environments to change both steric and electronic properties of the metal (**Figure 2.9**). These were allowed to react with epoxides and carbon monoxide under different reaction conditions to see if these modifications could impart the desired reaction chemistry. Unfortunately, these new systems showed similar reactivity to Brookhart's system, forming polyethers along with traces of diols and aldehydes.

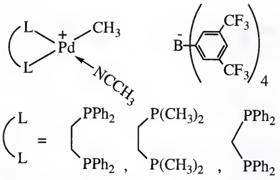


Figure 2.9 Additional cationic palladium complexes.

In general, the Pd(II) reactions produced products that contained mostly starting material or rearranged starting material. When the reaction mixture was poured into methanol or water, the corresponding diol was often formed. The diol probably results from opening the epoxide ring by the palladium complex, followed by addition of water to the opened epoxide. A diol can also be formed simply by adding an epoxide to acidic or basic aqueous solution, so it would seem that the cationic palladium complexes are again acting only as Lewis acids.

In some cases, the corresponding aldehyde product was formed, as indicated by a peak in the ^1H NMR spectrum around δ 9.7, and a weak carbonyl absorbance at 1725 cm^{-1} in the IR spectrum. The aldehyde is formed by an isomerism of the epoxide. Again the Lewis acidity of the Pd(II) complexes probably facilitates this rearrangement (Coxon 1970; Carey and Sundberg 1990).

Attempted Copolymerization of Epoxides with Carbon Monoxide Using a Cationic Titanium η^2-Acyl Complex

Since the cationic palladium complexes showed only ring opening of the epoxide rather than the desired insertion of the epoxide into a metal-acyl bond, a more electrophilic metal-acyl was employed. The complex $[Cp_2Ti(NCCH_3)COCH_3]^+BPh_4^-$ (Cp =

cyclopentadienyl) was chosen, because it contains an η^2-acyl which has increased electrophilicity at the carbonyl carbon due to coordination of the oxygen to the metal (Bochmann 1987) (**Figure 2.10**). Similar systems using zirconium are known to electrophilically ring-open cyclic ethers to form polyethers (Jordan 1991) (**Figure 2.11**). It was hoped that the increased electrophilicity at the carbonyl carbon would lead to reaction of the epoxide at the carbonyl.

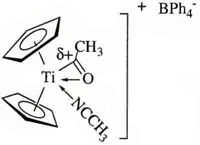


Figure 2.10 $[Cp_2Ti(NCCH_3)COCH_3]^+BPh_4^-$

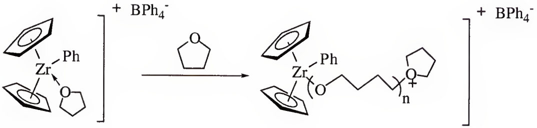


Figure 2.11 Reaction between $Cp_2Zr(THF)Ph^+BPh_4^-$ and THF forming polytetrahydrofuran.

No reaction was observed to occur between an epoxide and 1 atm of carbon monoxide at ambient temperature over the course of 2 days. After heating to 60 °C for 6 h the metal complex was observed to have decomposed, as indicated by numerous resonances in the Cp region of the ^1H NMR spectrum whereas the starting metal complex only had one resonance. The added energy may have been needed to displace the coordinated acetonitrile so the epoxide could coordinate. As soon as the epoxide coordinated, the extremely oxophilic metal may have deoxygenated the epoxide forming various titanium-oxo species.

Attempted Copolymerization of Epoxides with Carbon Monoxide Using Anionic Iron Complexes

Another possible system is based on the observation that strong nucleophiles ring-open epoxides to form alkoxides (Carey and Sundberg 1990) (**Figure 2.12**). Strong nucleophiles usually react with substituted epoxides at the least substituted site producing internal alkoxides similar to **2** (Parker 1959).

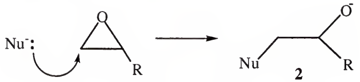


Figure 2.12 Reaction of nucleophiles with epoxides.

There are many nucleophilic metals in the literature which may be able to ring-open an epoxide to form a metalated alkoxide **2** which can then insert carbon monoxide to form one "unit" of polyester. Several transition metal systems have been directly observed to ring open an epoxide (Heck 1963; Rosenblum 1972). A requirement for this chemistry to succeed is for the oxygen on the metalated alkoxide to be able to insert into an electrophilic atom on the polymer chain covalently bound to the metal. A potential catalyst fitting this requirement would be an anionic metal-acyl complex. The acyl carbon of these complexes can be nucleophilically attacked by a metalated alkoxide formed by the ring-opening of the epoxide. By attacking the acyl carbon with the oxygen of the opened epoxide and eliminating the metal-acyl bond, only a metal-alkyl species remains. In the presence of carbon monoxide, an insertion of carbon monoxide will take place into the metal-alkyl bond returning the anionic metal-acyl complex (**Figure 2.13**).

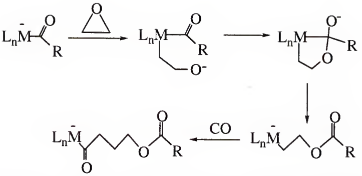


Figure 2.13 Proposed reaction scheme for polymerization of epoxides with carbon monoxide catalyzed by anionic transition metals.

Initial studies concerned the anionic systems $Cat^+[Fe(CO)_4COMe]^-$ (Cat = Li or PPN (bis(triphenylphosphoranylidene) ammonium)). These systems contain a formal negative charge on the iron nucleus which was hoped to be nucleophilic enough to ring open the epoxide. The reason two different cations were tried is that the literature (Semmelhack 1983; Miller 1987) has shown that the counterion has a large effect on the nucleophilicty of the iron atom in these systems. Each complex was mixed with epoxide and 1 atm of carbon monoxide at ambient temperature. No precipitate was formed after addition to methanol. After chromatography through alumina to remove catalyst followed by removal of all solvent, only starting material was recovered with no ester observed in the ^1H NMR spectrum.

Lack of reactivity may be due to the nature of anionic metal-acyl complexes. These complexes resemble organic enolates containing a resonance structure with the negative charge on the oxygen. In fact, this resonance structure is usually preferred for these complexes (Collman 1987) (**Figure 2.14**).

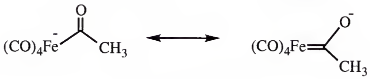


Figure 2.14 Resonance structures for $(CO)_4FeCOCH_3^-$.

In an attempt to create a more nucleophilic metal center the bimetallic anionic complexes, $Li^+[Fe_2(PPh_2)_2(CO)_6COMe]^-$ and $Na^+[Fe_2(CO)_8COMe]^-$ were tested as catalysts. Potentially in these complexes one iron would hold the negative charge to ring-open the epoxide, while the other iron would hold the acyl into which the opened epoxide would insert. Each complex was mixed with epoxide and 1 atm of carbon monoxide at ambient temperature. No precipitate was formed after addition to methanol, and after chromatography through alumina followed by removal of all solvent, no product was observed in the ^1H NMR spectrum.

Again the lack of reactivity seems to be caused by an equilibrium structure with the anion on the oxygen (Collman 1977; Finke 1979). The acyl oxygen is close enough to the anionic iron to be nucleophilically attacked by the iron to form an alkoxide. This alkoxide's oxygen anion is not nucleophilic enough to ring-open the epoxide. A similar equilibrium structure is seen with both metal complexes (**Figure 2.15**).

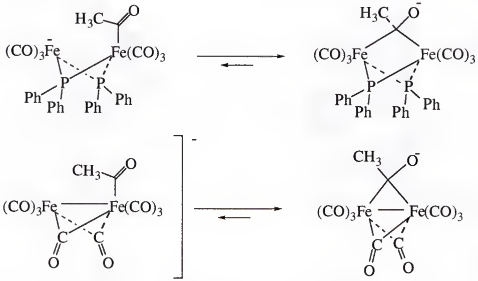


Figure 2.15 Equilibrium structures for bimetallic iron complexes.

To see if transition metal nucleophiles could ring-open an epoxide, the system $Na_2Fe(CO)_4 \cdot 1.5$ dioxane, known as the super nucleophile, was allowed to react with carbon monoxide and styrene oxide. After removal of solvent, the ^1H NMR spectrum of the product revealed both unreacted styrene oxide and styrene. A mechanism for the formation of styrene can be proposed (**Figure 2.16**).

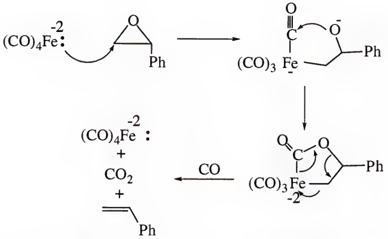


Figure 2.16 Proposed mechanism for the formation of styrene from styrene oxide.

In this mechanism, the epoxide is nucleophilically ring-opened by the iron anion. The anion formed on the oxygen then nucleophilically attacks a coordinated CO to from a metallalactone. This metallacycle then eliminates CO_2 and the olefin, styrene. This is the type of reactivity that is required with the iron-acyl species, but in those cases the iron is not nucleophilic enough to ring-open the epoxide.

Attempted Copolymerization of Epoxides with Carbon Monoxide Using Neutral Cobalt and Rhodium Complexes

In the literature, most of the examples of transition metal complexes which react with both carbon monoxide and epoxides involve cobalt (Murai 1989; Eisenmann 1961). Of these cobalt complexes, most are neutral, carbonyl-containing complexes. Presumably these complexes carbonylate epoxides by initial oxidative addition of the epoxide, followed by insertion of carbon monoxide and reductive elimination of the carbonylated product (**Figure 2.17**)

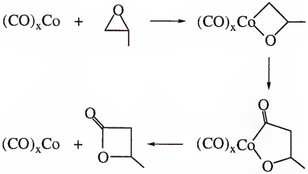


Figure 2.17 Proposed mechanism for carbonylation of epoxides with neutral cobalt complexes.

The complex Co(PPh3)(CO)2COMe **3** was chosen to examine as a catalyst because its acyl group has the potential of eliminating with an oxidatively added epoxide ring. It would be desirable to use a modified **3** without phosphines to complicate the reaction. However, without a phosphine, cobalt-acyl compounds are not stable or isolable, so **3** was used for this study. The proposed reaction would start with an oxidative addition of the epoxide by the cobalt complex forming a metalacyclooxitane (**Figure 2.18**). Reductive elimination of the oxygen with the acyl would then form a new cobalt-acyl group which would insert carbon monoxide to form a new cobalt-acyl group to continue propagation.

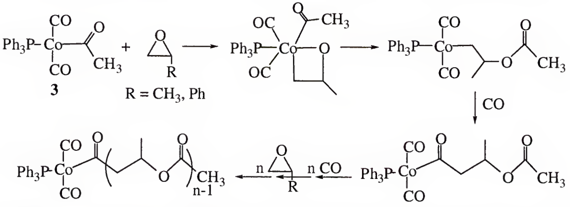


Figure 2.18 Proposed reaction scheme for polymerization of epoxides with carbon monoxide catalyzed by a cobalt-acyl complex.

Complex **3** was stirred with propylene oxide and 1 atm of CO at ambient temperature for 24 h. No precipitate was formed from addition to methanol, and after removal of all solvent, no ester product was seen by either ^{1}H NMR or IR spectroscopy. This reaction was repeated at 100 atm and at 60 °C for 24 h with the same lack of reactivity. It would seem that **3** is not a reactive enough complex to activate an epoxide.

Other systems were tested with epoxides and carbon monoxide to try to increase the reactivity at the metal center. Two rhodium complexes were prepared to see if rhodium is more reactive toward epoxide activation than cobalt. The complexes $(PPh_3)_3RhMe$, and $(CODRhCl)_2$, (COD = 1,5-cyclooctadiene) were each mixed with epoxide and carbon monoxide at ambient temperature for 24 h. Neither reaction formed a precipitate upon addition to methanol, and after removal of all solvent, neither showed ester in its ^{1}H NMR or IR spectrum. Again it seems that there is not enough nucleophilicity at the metal center in these rhodium complexes to react with the epoxide.

Copolymerization of Epoxides with Carbon Monoxide Catalyzed by Cobalt Complexes with Alkylaluminum Cocatalysts

There are some rare cases in the literature where the direct copolymerization of carbon monoxide and epoxides is reported. Furukawa and coworkers (1965) claim to have successfully made polyesters from carbon monoxide and epoxides using a catalyst system of $Co(acac)_3$ (acac = acetylacetonate) and triethyl aluminum. The polymeric product obtained from the reaction of propylene oxide with 100 atm carbon monoxide at 100 °C using this catalytic system seems to show no regioselectivity for the carbon monoxide insertion into the oxygen carbon bond of the epoxide. The polymer was reported to consist of two different ester groups along with polyether repeat units (**Figure 2.19**).

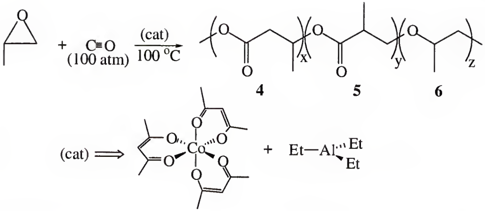


Figure 2.19 Furukawa's polyester synthesis from epoxides and carbon monoxide.

Since Furukawa's reaction was the first reported polymerization of an epoxide with carbon monoxide the reaction was repeated as a starting point for understanding the chemistry, although the report gives only sketchy experimental details. The reaction was undertaken in glass vials which were place inside a Parr™ high pressure reactor. Initially, one equivalent of Co(acac)$_3$ was placed the vial along with 100 equivalents of propylene oxide forming a green solution. One equivalent of triethyl aluminum was added to this solution causing a dramatic color change from green to red along with vigorous bubbling, although no heat evolution was observed. This vial was sealed inside the reactor and the reactor was pressurized to 100 psi CO. The reactor was then heated to 100 °C and the mixture was stirred by way of a magnetic stirplate. After two days, heating was stopped and the pressure released. The resulting product was a viscous oil with a M_w=3000 determined by GPC versus polystyrene standards, compared to M_w=800 which Furukawa reported. The ^{1}H NMR spectrum of the product is nearly identical to a published spectrum of poly-β-hydroxybutyrate (Jedlinski 1991) with major resonances at δ 1.28, 2.50, and 5.25 which correspond to the CH_3, CH_2, and CH protons, respectively, of repeat unit **4** of Furukawa's polymer (**Figure 2.20**). The ^{13}C NMR data also show resonances which agree with repeat unit **4** at δ 19.8, 40.8, 67.6, and 169.2 which correspond to the CH_3, CH_2, CH, and C=O carbons respectively. Very little of what Furukawa claimed as repeat

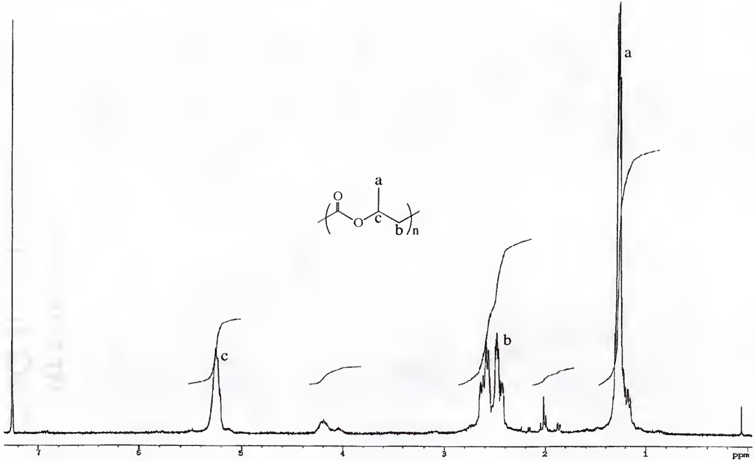


Figure 2.20 ^{1}H NMR of Poly-β-hydroxybutyrate made from propylene oxide and carbon monoxide catalyzed by Co(acac)$_3$ and AlEt$_3$.

units **5** and **6** appeared in this product, making the catalyst system of $Co(acac)_3/AlEt_3$ much more selective than reported. The conditions for this reaction are fairly constrained. Normally, this reaction is run at 100 atm CO and 100 °C for 48 h. Lowering the CO pressure by only 20% results in the formation of no polymeric product. Lowering the temperature below 75 °C also results in the formation of no polymeric product.

More recently Kurachi (1994) has also claimed to have produced poly-β-hydroxybutyrate. This synthesis is reported to proceed from the reaction of propylene oxide with 100 atm of carbon monoxide at 75 °C in the presence of $Co_2(CO)_8$ for 10 h. Molecular weight of the resultant polymer is claimed to be 10000. An attempt was made to repeat this reaction, as was done for Furukawa's system, although no polymeric products were isolated.

Looking at Furukawa's polymerization system of $Co(acac)_3$ and triethyl aluminum, it is not obvious what the active catalyst is. When $Co(acac)_3$ and triethyl aluminum are mixed, the green $Co(acac)_3$ solution becomes red accompanied by vigorous bubbling. Several studies have been carried out to try to elucidate the active species. Tamai and coworkers (1965) have concluded that initially the cobalt complex is reduced to $Co(acac)_2$ and the aluminum complex is transformed to $AlEt_2(acac)$. These complexes then go on to further react forming finely divided cobalt metal, $Al(acac)_3$, ethane and ethylene. Nicolescu and coworkers (1966) have concluded that the cobalt species actually gets reduced only to $Co(acac)_2$, although $Co(acac)_2$ by itself is not an active species for the polymerization. Obviously, elucidation of the actual active species is not trivial.

Some clues concerning the nature of the catalyst system can be discussed. One possibility is that the purpose of the triethyl aluminum is to reduce the cobalt to a cobalt (0) or (-1) species which carbonylates the epoxide into a lactone as in the Drent and Heck systems. The lactone can then be polymerized by the Lewis acidic aluminum. Another option is that the triethyl aluminum alkylates the cobalt to a cobalt (I) or (III) alkyl which inserts CO to form an acyl. This cobalt-acyl compound then oxidatively adds the epoxide which reacts with the acyl to form an ester.

A common compound formed from the reduction of cobalt salts in a carbon monoxide atmosphere is $Co_2(CO)_8$ (Szabó 1965). Despite the uncertainty of the mechanism, it can be concluded that $Co_2(CO)_8$ is not the catalytic species in this polymerization. Under identical reaction conditions to those used for Furukawa's system, $Co_2(CO)_8$ does not carbonylate propylene oxide to produce an ester of any kind (**Figure 2.21**).

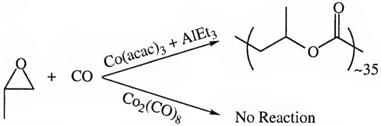


Figure 2.21 Products formed from Furukawa's catalyst system and $Co_2(CO)_8$.

Several experiments were run to test the reactivity of the components of Furukawa's system. First, it was made clear that neither of the catalyst's components individually acts as the catalyst. $Co(acac)_3$ was mixed with propylene oxide and 100 atm of carbon monoxide at 100 °C. After 2 days no reaction was observed. Similarly, triethylaluminum was mixed with propylene oxide and 100 atm of carbon monoxide at 100 °C. After 2 days only polypropylene oxide was recovered.

Secondly, the effect of the identity of the aluminum component was tested. Diethylaluminum chloride, trimethylaluminum, and methylalumoxane (MAO) were chosen as alternate alkylaluminum sources. Using the same reaction conditions that produced polyester with triethylaluminum these alkylaluminums were tested with $Co(acac)_3$. None of the alkylaluminum compounds cocatalyzed the formation of polyester as selectively as triethylaluminum. In each case, the product formed was a low molecular weight mixture of polyester and polyether, with the majority being polyether (**Figure 2.22**).

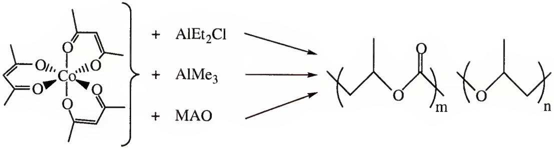


Figure 2.22 Reaction of Co(acac)$_3$ with different alkylaluminums.

Thirdly, the cobalt component was altered to see what effect this had. Cobalt octacarbonyl, cobalt chloride, and a cobalt acyl compound were chosen as alternate cobalt sources. Using the same reaction conditions that produced polyester with Co(acac)$_3$ these cobalt complexes were tested with triethyl aluminum. None of the cobalt complexes catalyzed the formation of polyester as selectively as Co(acac)$_3$. Again, the product formed was a mixture of polyester and polyether, with the majority being polyether (**figure 2.23**). It is not clear whether these mixtures of polyester and polyether are mixtures of homopolymers or are copolymers.

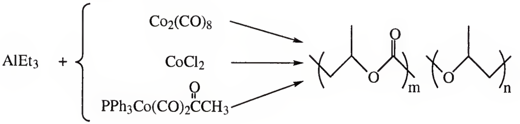


Figure 2.23 Reaction of triethyl aluminum with cobalt complexes.

Three additional transition metal complexes were used in the place of cobalt with triethyl aluminum under identical conditions to those used to form polyester with Co(acac)$_3$. [Ni(acac)$_2$]$_2$, [(COD)RhCl]$_2$, and Fe(acac)$_3$ showed no ability of catalyze polyester formation with only polyether observed as a product (**Figure 2.24**).

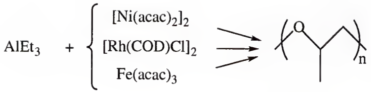


Figure 2.24 Reaction of triethyl aluminum with nickel, rhodium and iron complexes.

It is evident from these test reactions is that there is a specific active species being formed in the Furukawa system, not generic finely divided metal or a simple metal carbonyl. So far it appears that cobalt is the only transition metal able to catalyze this reaction. Also the aluminum cocatalyst is specific in this reaction. Triethyl aluminum is the only alkylaluminum to give solely polyester in this reaction.

Copolymerization of Epoxides with Carbon Monoxide Using Neutral Cobalt Complexes

Since the mixture of $Co(acac)_3$ and $AlEt_3$ is the only system which successfully copolymerizes carbon monoxide with epoxides, our studies turned to isolable cobalt systems derived from the reaction of $Co(acac)_3$ and $AlEt_3$.

Yamamoto (1975, 1976) has synthesized a series cobalt alkyl complexes by reacting $Co(acac)_3$ and $AlEt_2OEt$ in the presence of phosphine ligands (**Figure 2.25**). Of special interest with these compounds are the extreme differences caused by subtle changes in ligands. With triphenylphosphine as a ligand, a cobalt (I) compound **7** is formed with a π-bound ethylene. With dimethylphenylphosphine as a ligand, a cobalt (III) compound **8** is formed with two ethyl groups σ-bound to the metal. The larger cone angle of the triphenylphosphine versus dimethyl phenyl phosphine appears to induce β-hydride elimination of the ethyl groups leaving only a coordinated ethylene. Both of these complexes contain acetylacetone as a ligand which might be expected in the active species generated from $Co(acac)_3$ and $AlEt_3$.

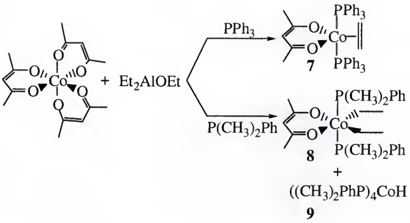


Figure 2.25 Products of $Co(acac)_3$ with Et_2AlOEt and phosphine.

During the synthesis of the dimethylphenylphosphine complex another compound, $HCo(P(CH_3)_2Ph)_4$ (**9**), was isolated, possibly formed from decomposition of **8**. All three of these complexes are potentially similar to the active species formed from the Furukawa system. However, when any of these three complexes was allowed to react with propylene oxide and carbon monoxide, only unreacted starting material was recovered. Although none of these complexes catalyzed the formation of polymer, any of these complexes may still be close to the active catalytic species in Furukawa's system. Phosphines are known to poison the catalytic activity in many systems and the presence of phosphines in these complexes may do the same.

Since phosphines may be inhibiting the catalytic activity of these complexes, derivatives without phosphines were synthesized. The syntheses of these compounds were still based on the reaction of $Co(acac)_3$ with triethylaluminum. Bönnemann and coworkers (1984) prepared the compound, [(1,2,5,6-η)-1,5-cyclooctadiene][(1,2,3-η)-2-cycloocten-1-yl]cobalt **10**, from the reaction of $Co(acac)_3$ and triethylaluminum in the presence of 1,5-cyclooctadiene. Alternatively, this compound can be prepared from the reaction of $CoCl_2$ with Na, 1,5-cyclooctadiene and pyridine (Otsuka 1968; Cushing 1977) (**Figure 2.26**).

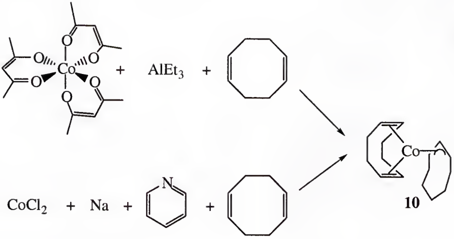


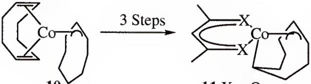
Figure 2.26 Syntheses of **10**.

Compound **10** was exposed to propylene oxide and 100 atm of carbon monoxide at 100 °C. After 2 days, heating was stopped and pressure released to reveal a red viscous oil. The ^{1}H NMR spectrum showed this oil was consistent with poly-β-hydroxybutyrate, although the spectrum showed a significant amount of what Furukawa reported to be an ether repeat unit. Similar to Furukawa's Co(acac)$_3$ and triethylaluminum system, the molecular weight of this product was 2000. The special feature of this catalyst system is the absence of the alkylaluminum cocatalyst. This seems to indicate that in Furukawa's system the purpose of triethylaluminum is strictly as an alkylating/reducing agent although it may also function as a scavenger for impurities in the reaction mixture. In metallocene based polymerizations, alkyl aluminum reagents function as both cocatalysts and as scavengers for removing water and other impurities. This cobalt complex also potentially allows for easier mechanistic study because now there is a well defined precatalyst. Compound **10** has been shown to coordinate CO reversibly under 1 atm of CO (Otsuka 1969), which maybe the initial step in the catalytic cycle. One of the drawbacks to this compound is that it is very air sensitive and thermally unstable, and with even a little decomposition, paramagnetic material forms making NMR study difficult.

The conditions for polymerization using **10** were varied to see if any difference in reactivity was observed. As with Furukawa's system, **10** only remained active above 80 °C and 100 atm CO. Increasing the CO pressure to 300 atm did not significantly change the activity of **10**. The reaction was also run in supercritical carbon dioxide in hopes that the solubility of CO in the reaction mixture would be increased and consequently the activity of the catalyst would be increased as well (Noyori 1995). It was also postulated that CO_2 could be incorporated into the product creating an interesting copolymer containing ester and carbonate repeat units. No increase in activity of the catalyst or CO_2 incorporation into the polymer was detected. The product was similar to that formed from **10** under normal conditions, except that a significant amount of β-butyrolactone was observed along with poly-β-hydroxybutyrate. Perhaps the butyrolactone was produced during a side reaction which was magnified by the CO_2 environment. Another possibility is that butyrolactone is being produced in every polymerization involving **10**. The lactone then homopolymerizes to make poly-β-hydroxybutyrate. Supercritical carbon dioxide may hinder this homopolymerization leading to observation of the lactone.

Several compounds were synthesized from compound **10** to test their ability as catalysts (**Figure 2.27**). Due to reaction conditions, all of these are Co (III) complexes as opposed to the Co (I) metal center in **10**. These compounds were chosen because they contain an acac or equivalent ligand to mimic a potential compound made from the reaction of $Co(acac)_3$ and triethyl aluminum. Both the steric and electronic environments of the acac ligand were adjusted to see what effect they had on any catalytic activity. These complexes will be discussed in further detail in chapter 4.

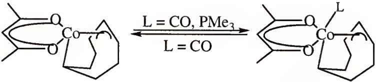
Compound **11** is green but turns red upon addition of ligand, similar in color to the species formed from the reaction of $Co(acac)_3$ with triethyl aluminum. Compound **11** shows a reversible coordination of CO and an irreversible coordination of PMe_3. Initially it was thought that CO inserted into the allyl bond of **11** due to loss of molecular symmetry in the ^1H NMR spectrum. Unfortunately, the molecule formed decomposed after five minutes making analysis using ^{13}C NMR spectroscopy difficult to determine if a metal acyl was formed. When PMe$_3$ was added to **11** a stable compound **13** with a similar ^{1}H NMR spectrum as that of **11** with CO was observed (**Figure 12.28**). Whereas CO has the ability to insert into the metal allyl bond, PMe$_3$ cannot insert into the metal alkyl bond. The similarity of ^{1}H NMR spectra of the two reactions implies a similar product, most likely simple coordination of ligand. It may be that after the initial coordination of CO, insertion does occur, which leads to decomposition of the compound. When PMe$_3$ is used as a ligand insertion cannot occur, preventing decomposition.



10

11 X = O
12 X = NPh

Figure 2.27 Derivatives made from **10**.



11

13 L = PMe$_3$

Figure 2.28 Coordination of ligands to **11**.

When compounds **11** and **12** were allowed to react with propylene oxide and CO using the same conditions as for **10**, a products containing peaks in the ^{1}H NMR spectrum consistent with poly-β-hydroxybutyrate were formed (**Figure 2.29**). The polymer formed was not as well defined as in the case of **10**, due to increased formation of polyether. Compound **11** was much more active than **12** in formation of the polymer, converting twice as much propylene oxide as **12**.

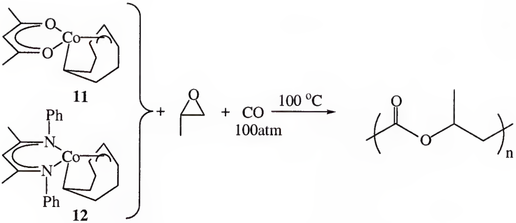


Figure 2.29 Poly-β-hydroxybutyrate formation using Co (III) catalysts.

It should be noted that since the active catalyst species is not known it is possible that **10**, **11**, and **12** get reduced to a similar species in the reaction system. Other cobalt complexes containing the η1-η3 cyclooctenyl ligand have been shown to isomerize to form (1,2,5,6-η)-1,5-cyclooctadiene complexes upon heating (Bönnemann 1988). Possibly **11** and **12** isomerize in the reaction mixture to make species similar to **10**.

Two types of reaction mechanisms for the polymerization can be proposed given our observations (**Figure 2.30**). In one mechanism, polymerizaion is initiated by a low oxidation state cobalt alkyl species. This species coordinates carbon monoxide, which then inserts to form an acyl. Propylene oxide then coordinates, followed by insertion to form an ester linkage and reformation of the cobalt alkyl. Propagation of this mechanism forms poly-β-hydroxybutyrate. The alternate mechanism again initiates by a low oxidation state cobalt species. Propylene oxide then coordinates, followed by oxidative addition to form a metallacycle. Coordination of carbon monoxide and insertion to form a metallalactone follows. Finally reductive elimination forms butyrolactone, as observed in supercritical carbon dioxide, which can homopolymerize to form poly-β-hydroxybutyrate. Distinguishing between the two potential mechanisms is not trivial. The requirement for high pressure of CO severely limits the type of analytical techniques which can be employed to determine the mechanism. At first glance, it might seem straight forward to add labeled butyrolactone to the reaction mixture. If label is incorporated into the polymer then polymerization goes by mechanism 2. Unfortunately, it is equally likely that labeled butyrolactone can oxidatively add to the active catalyst in mechanism 1. This type of oxidative addition of lactones have been observed in other late transition metal systems (Puddephatt 1988). After a reductive addition step, label is incorporated into polymer.

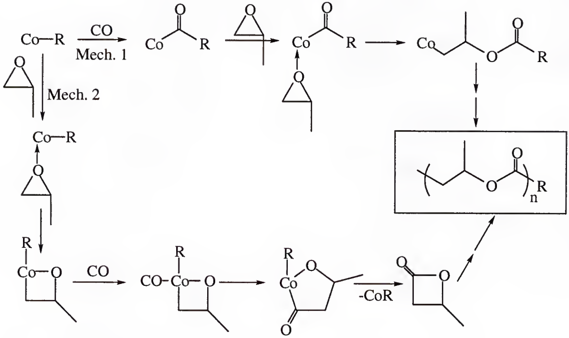


Figure 2.30 Proposed mechanisms for polyester polymerization.

The reaction of epoxides with carbon monoxide using these cobalt compounds can be modified to produce a small molecule which may be a useful monomer. There are several benefits to making a monomer instead of a polymer. Creating a monomer such as methyl 3-hydroxybutyrate eliminates the need to make a polymer in one step, and the small molecule can be isolated and purified by standard organic methods. This monomer can then be polymerized by a condensation reaction to make poly-β-hydroxybutrate. Molecular weights can be controlled in this condensation polymerization allowing specific molecular weights to be produced.

One equivalent of methanol was added to a reaction mixture containing propylene oxide and **11**. This reaction mixture was pressurized to 100 atm CO and heated to 100 °C. After 2 days, heating was stopped and pressure released. No polymer was formed. Instead a red liquid was recovered. After vacuum distillation, methyl 3-hydroxybutyrate was isolated in a 34% yield (**Figure 2.31**). Although no polymerization of methyl 3-hydroxybutyrate has been achieved as of yet, this molecule contains an alcohol and ester which have been used to successfully polymerize other monomers (Carothers 1933).

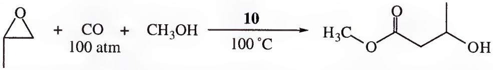


Figure 2.31 Formation of methyl 3-hydroxybutyrate from propylene oxide, carbon monoxide and methanol.

Summary and Conclusions

Several observations were made as to what qualities an effective catalyst for the copolymerization of an epoxide with carbon monoxide would have. Cationic transition metal complexes are too electrophilic to allow any chemistry besides ring opening polymerization or isomerization of the epoxide. Modification of the ligand system around these metal complexes does not significantly change their reaction chemistries. Anionic transition metal acyl complexes lack the nucleophilicity to ring open the epoxide. The complexes which are nucleophilic enough to open the epoxide ring lack the proper substituents to propagate a polymer chain. Neutral transition metal complexes initially also showed no reactivity toward the proposed polymerization.

Unexpectedly, the system of $Co(acac)_3$ and $AlEt_3$ displays the remarkable ability to copolymerize propylene oxide and carbon monoxide to product low molecular weight poly-β-hydroxybutyrate. The polymer shows predominately one repeat unit, which makes it a much more well defined polymer than reported. The catalyst mixture has been shown to be specific in both cobalt and alkylaluminum component as well as temperature and pressure. Compound **10**, a complex which can be prepared using $Co(acac)_3$ and $AlEt_3$, also shows the ability to catalyze the copolymerization. The discovery that **10** is a catalyst now allows study of a well defined system and presents the opportunity to develop derivatives of **10** which may be better catalysts. The initially prepared derivatives such as **11** and **12** already show promise as catalysts, although they are not as reactive as **10**.

Instead of making a polymer in one step, a monomer, methyl 3-hydroxybutyrate, can be formed by addition of methanol to the reaction mixture. This molecule can be isolated by distillation in decent, although unoptimized, yields. Future work to polymerize this monomer must be undertaken to see if it is a viable route to poly-β-hydroxybutyrate.

CHAPTER 3
POLYESTER SYNTHESIS USING CARBOALKOXYLATION

Carboalkoxylation

There are many ways to create ester functionalities using transition metal catalysts (Perri 1990, 1992; Sugi 1996; Inoue 1996). One such reaction is the carboalkoxylation reaction. Carboalkoxylation involves the reaction of an olefin, an alcohol, and carbon monoxide react to produce an ester (**Figure 3.1**).

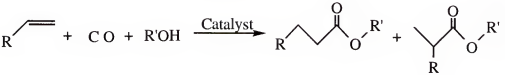


Figure 3.1 Ester synthesis by carboalkoxylation.

Several different transition metal systems are known to catalyze this reaction (Knifton 1976b; Milstein 1982) but the predominant catalyst systems employ palladium. The conditions for this reaction are varied. Alper and coworkers (1983) have shown the utility of the $PdCl_2/CuCl_2/HCl/O_2$ catalyst system. This system generates esters and carboxylic acids with up to 100% yield, and using α,ω-dienes a 98% conversion into the diester is achieved. Given the high reactivity of dienes, it would be anticipated that polymers could potentially be generated if a diene and a diol were used. Unfortunately, using diols with the dienes in a 1:1 ratio severely lowers yields of diesters with no reported polymeric product (**Figure 3.2**).

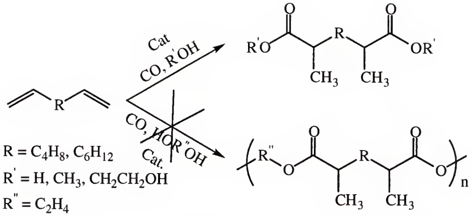


Figure 3.2 Reaction of dienes with alcohols using Alper's catalyst system.

Alper (1985) also reports that this catalyst system will convert unsaturated alcohols to lactones in up to 60% yields. This system offers the ability to use relatively mild reaction conditions, 1 atm of CO pressure at room temperature, however the use of O_2 in a system containing CO adds an element of danger to this reaction.

Drent and coworkers (1993) have utilized carboalkoxylation to make methyl methacrylate from propyne, carbon monoxide, and methanol (**Figure 3.3**). The catalyst system used was a mixture of $Pd(OAc)_2$, $2\text{-}PyPPh_2$ (Py = pyridyl), and a Brønsted acid. The reaction took place at 45 °C and 60 bar of CO, and a 99% selectivity to methyl methacrylate was achieved.

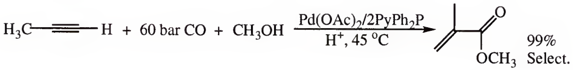


Figure 3.3 Formation of methyl methacrylate from propyne, carbon monoxide and methanol.

The conditions, catalyst, and substrates for carboalkoxylation can be altered to allow other carbonylation products. Knifton (1980) has shown that using Wilkinson's catalyst at 150 °C with 136 atm of CO, allyl amines can be converted to lactams (**Figure 3.4**).

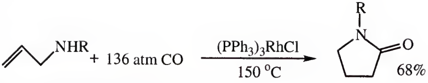


Figure 3.4 Lactam formation from an allyl amine.

An interesting reaction has been reported when 3-buten-1-ols are used as substrates (Tamaru 1991). These substrates undergo a bis-carbonylation producing both a lactone ring and a pendant ester in high yields (**Figure 3.5**).

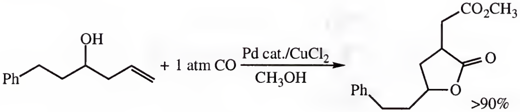


Figure 3.5 Bis-carbonylation of a 3-buten-1-ol.

It has been postulated that this bis-carbonylation reaction proceeds through initial formation of a palladium-acyl with coordinated olefin. Coupling of the olefin with the acyl produces a palladium-alkyl species with a coordinated ester. Insertion of carbon monoxide into the metal-alkyl followed by elimination with alcohol produces the organic product (**Figure 3.6**).

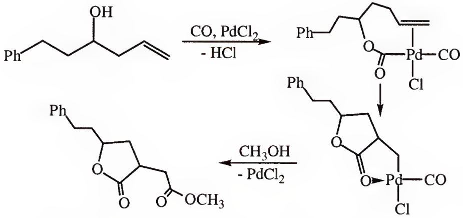


Figure 3.6 Proposed mechanism for carboalkoxylation of a 3-buten-1-ol.

Mechanism of Carboalkoxylation

The mechanism of the palladium catalyzed carboalkoxylation has been the subject of debate in the literature (Toniolo 1990; Milstein 1988). Two possible mechanisms exist to explain the formation of products. One relies on the initial formation of a palladium hydride species (**Figure 3.7**). Olefin then coordinates to the metal and inserts into the palladium-hydride bond. Carbon monoxide coordination and insertion into the palladium-alkyl bond follows. Regeneration of the palladium hydride and elimination of the ester results from nucleophilic attack of the palladium-acyl bond by an alcohol.

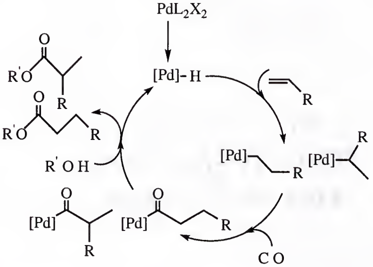


Figure 3.7 Proposed mechanism for carboalkoxylation based on palladium hydride formation.

The other possible mechanism starts with formation of a palladium carbonyl complex (**Figure 3.8**). Nucleophilic attack on the carbonyl by the alcohol forms a palladium ester complex. An olefin then inserts into the palladium-ester bond forming a palladium alkyl species. The catalyst is then reformed by protonation of the alkyl species forming the ester and coordination of carbon monoxide.

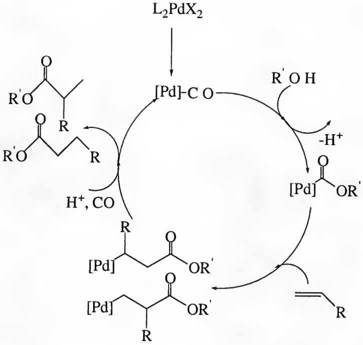


Figure 3.8 Proposed mechanism for carboalkoxylation based on palladium carbonyl formation.

There is evidence that supports both mechanisms. Toniolo and coworkers (1990) have seen that palladium acyls react with alcohols stoichiometrically to produce esters, lending evidence for the first mechanism. The formation of a palladium hydride can be accounted for by the presence of alcohol in the reaction. Alcohols are known to react with transition metal halides to produce hydrides (Collman 1987).

Others have shown that in the reaction of carbon monoxide with platinum alkyl alkoxides, carbon monoxide preferentially reacts with the platinum-alkoxide bond over the platinum-alkyl bond, lending evidence for the second mechanism (**Figure 3.9**) (Bryndza 1985). It is likely that the mechanistic pathway depends on the specific catalyst system. Different catalyst systems will have different preferences toward one mechanism over the other.

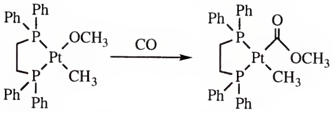


Figure 3.9 Insertion of carbon monoxide into a platinum alkoxide bond.

The regiochemical preference of the carboalkoxylation reaction is predominately toward production of a branched product. This preference occurs during the insertion of the olefin in either mechanism, although the first mechanism accounts for the predominance of the branched better than the second mechanism. Although ancillary ligands have a strong influence over the nature of the hydride, late transition metal hydrides tend to be acidic in nature, more like an H^+ than an H^- (Collman 1987), while early transition metal hydrides tend to be more hydridic (Labinger 1978). Therefore, when the olefin inserts into the metal-hydride bond, the olefin acts as though it is being protonated, producing a Markovnikov addition product with the metal on the more substituted carbon (**Figure 3.10**). After insertion of carbon monoxide and elimination by alcohol the branched ester is formed.

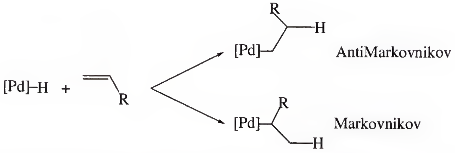


Figure 3.10 Regiochemistry of olefin insertion into palladium-hydride bond.

There are some transition metal systems which selectively produce linear product. Knifton (1976) and Lee (1995) have developed systems using palladium or platinum with various ligands and cocatalysts which give linear esters. In the case of palladium, the best precatalyst system is a mixture of bis(triphenylphosphine)palladium dichloride with tin chloride or germanium chloride as a cocatalyst (**Table 3.1**).

Table 3.1 Linear ester yields for various catalyst systems.

Catalyst	Cocatalyst	Cocatalyst Equivalents	Best Conversion %	% Linear Ester
$[(C_6H_5)_3P]_2PdCl_2$[a]	——	—	93	58
$[(C_6H_5)_3P]_2PdCl_2$[a]	$SnCl_2$	10	96	87
$[(C_6H_5)_3P]_2PdCl_2$[a]	$GeCl_2$	10	96	88
$[(C_6H_5)_3P]_2PdCl_2$[a]	$PbCl_2$	10	87	44
$[(C_6H_5)_3P]_2PdCl_2$[a]	$SnClPh_3$	10	7.9	89
$PdCl_2$[b]	PPh_3/HCl	4/4	98	15
$PdCl_2$[b]	DPPP	4	17	88
$PdCl_2$[b]	$CuCl_2/PPh_3$	2/4	99	1

a.Conditions: 102 eq 1-heptene, 7.4×10^2 eq MeOH, 240 atm CO, 80 °C, 6 h.
b.Conditions: 102 eq 4-methylstyrene, 4 ml MeOH, 41 atm CO, 100 °C, 4 h.

Tin chloride is the favored cocatalyst for the investigations presented within. The exact active catalytic species in the system of $[(C_6H_5)_3P]_2PdCl_2/SnCl_2$ is not known. The species $[(C_6H_5)_3P]_2Pd(SnCl_3)Cl$ and $[(C_6H_5)_3P]_2Pd(SnCl_3)_2$ have been recovered from reaction mixtures. Knifton proposes that the active catalytic species is $[(C_6H_5)_3P]_2Pd(SnCl_3)H$. The selectivity of Knifton's catalytic systems toward linear ester has been explained in two ways. Firstly, the catalyst contains bulky phosphines along with a large tin trichloride group. This steric bulk forces the olefin insertion to produce the least sterically encumbering metal-alkyl group, one which would be formed from a linear insertion. Secondly, it is postulated that the tin trichloride group alters the electronics of the transition metal it is attached to. This changes the nature of the metal hydride, making it more hydridic, which in turn leads to an anti-Markovnikov insertion product.

Polyester Synthesis Using Dienes and Diols

The adaptation of the carboalkoxylation reaction to make polyesters is straight forward. By replacing the monofunctional olefins and alcohols with unconjugated terminal dienes and terminal diols polymers can be produced. The difunctionality of the monomers allows ester synthesis at both ends of the monomers to product polymers. The use of carboalkoxylation to produce polymers using dienes and diols has been only reported once (Drent 1991b). Drent produced low molecular weight polymers by using a catalytic mixture of palladium acetate, an excess of phosphine ligand and a sulfonic acid with a pKa below 2. The polymers produced contain both linear and branched alkyl backbone repeat units. This type of polymerization is a step addition polymerization. Since the reaction is an addition type, the polymerization cannot be aided by removal of a condensate.

Syntheses of Poly(alkylene dodecanedioate)s

The syntheses of all of the poly(alkylene dodecanedioate)s were carried out in the same manner. Three different polymers were synthesized from the reaction of carbon monoxide with decadiene and a diol, either ethylene glycol, 1,3-propane diol, or 1,4-butanediol. In an inert atmosphere glove box, 1 equivalent bis(triphenylphosphine) palladium dichloride and 5 equivalents tin chloride hydrate were added to a glass vial equipped with a magnetic stirbar. To the vial were then added 200 equivalents of 1,9-decadiene and 200 equivalents of a diol. Acetone (20 mL) was then added to the vial and the vial was sealed using a cap with a hole to allow for changes in pressure. At this point the reaction mixture was red. The vial was then placed in the Parr high pressure reactor and the reactor was sealed. The reactor was removed from the glove box, pressurized to 1500psi with carbon monoxide and heated to 75 °C. After 2 days pressure was released and the contents of the vial were poured into stirring hexanes forming a white semisolid precipitate (**Figure 3.11**).

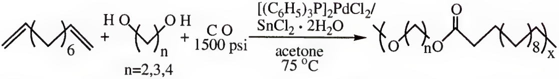


Figure 3.11 Formation of poly(alkylene dodecanedioate)s.

Poly(ethylene dodecanedioate), **13**, was the product of the copolymerization of 1,9-decadiene with ethylene glycol and carbon monoxide. The M_w of the polymer was 900 with a polydispersity of 1.4 in reference to polystyrene standards. The GPC trace shows a bimodal distribution, evidence for the formation of cyclics and straight chains (Wagener 1993). The consistency of the polymer is that of a semisolid waxy material. Poly(trimethylene dodecanedioate), **14**, is the product of the copolymerization of 1,9-decadiene with 1,3-propane diol and carbon monoxide. The M_w of this polymer is 2000 with a polydispersity of 1.4. Again the GPC trace shows a bimodal distribution, evidence for the formation of cyclics and straight chains. Poly(tetramethylene dodecanedioate), **15**, is the product of the copolymerization of 1,9-decadiene with 1,4-butane diol and carbon monoxide. The M_w of this polymer is 1000 with a polydispersity of 1.6. This too showed a bimodal distribution in the GPC.

Evidence for a linear backbone polymer can be seen in the ^1H NMR spectra of the polymers. The resonances at δ 2.3 which correspond to the methylene α to the carbonyl integrate to an even number of protons, with a triplet splitting pattern indicating α -CH_2- group next to only another -CH_2- group which would be expected for a linear ester. A branched ester would be expected to display a resonance which integrates to an odd number and is split into a triplet of quartets. The fact that no such resonance appears in the ^1H NMR suggests that the amount of branched product is very small, relative to linear product.

End-group analysis is a good method for determining number average molecular weight (M_n) of polymers. There are usually two end groups for each linear polymer molecule, so the number of polymer molecules can be deduced. From the ratio of weight of the polymer mixture to the number of polymer molecules, the M_n can be determined. End groups arise from the consumption of one of the monomers in the polymerization. When one monomer is used up, the other is the last to react with the growing polymer. Since the monomers are bifunctional, one end reacts with the polymer while the other is left at the end of the polymer (**Figure 3.12**). The end group for these polymers should be a mixture of olefinic and alcoholic functionalities.

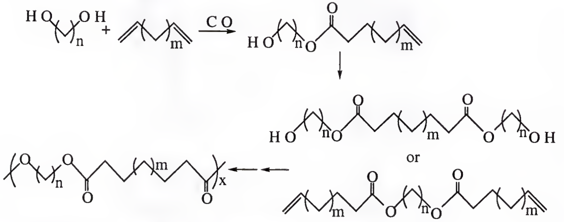


Figure 3.12 Polymer growth showing endgroup formation.

The ^{1}H NMR spectra show very little olefinic signal with a larger amount of alcoholic signal. Ideally, there should be an equal amount of olefinic to alcoholic end group. Neither signal corresponds to an abundance which should exist based on GPC determined molecular weights. The lack of equality in end groups can be explained in a few ways. First, the ratio of diene to diol at the start of the reaction may not equal due to experimental error. Second, the olefin end groups could have been masked. Hydrogenation of the olefin end groups could have occurred. There are hydrogen sources in the reaction mixture, alcohol and acetone, and the catalyst is palladium, a metal known to hydrogenate alkenes. The fact that the amount of either end group does not correlate to the observed molecular weight can be more easily explained. In step polymerizations, the polymer produced is not always a straight chain. Often an amount of cyclic products are produced. This occurs because the polymer that is reacting with the catalyst contains a reactive site at its other end which can back bite with the catalyst and eliminate a cyclic product (**Figure 3.13**). Obviously, this cyclic polymer has no ends, and as such cannot contain end groups. The bimodal distribution of the GPC seems to confirm the existence of cyclics in the polymer.

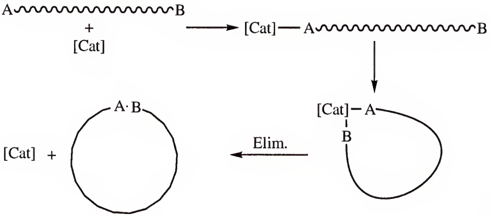


Figure 3.13 Formation of cyclic oligomers in a step reaction.

This backbiting reaction can be limited by elimination of a solvent in a polymerization reaction. In a solvent system the concentration of monomer near the catalyst is significantly smaller than in a solventless system. Since there is a low concentration of monomer near the catalyst, the dangling reactive end of the monomer which is reacting with the catalyst is held near the catalyst making it much more likely to react with the catalyst forming a cyclic product. Unfortunately, in the case of the carboalkoxylation polymerization a solvent, acetone, is needed for solublizing the comonomer system. The reaction will not work in the absence of solvent.

The cyclization products can also account for the molecular weights of the polymers. When the polymer cyclizes its end groups react with each other, eliminating them. With no end groups available, the polymer can no longer build on itself with other monomers or oligomers to make itself larger. Another limiting factor to polymer size can be seen in the ^{1}H NMR of the polyesters. The olefin endgroup signal consists not only of terminal olefin, but also internal olefin. The production of internal olefin is not unexpected, considering the possibility of a metal hydride species in the reaction mixture.

The mechanism for the isomerization of the olefin is compatible with the polymerization mechanism (**Figure 3.14**). The olefin inserts into the metal-hydride bond forming the preferred liner metal alkyl species and to a lesser extent the branched metal alkyl species. While β-H transfer from the linear metal alkyl reproduces the terminal olefin, β-H transfer from the branched metal alkyl can produce the terminal olefin, but favors production of the more stable internal olefin. Since internal olefins are much less reactive to carboalkoxylation than terminal olefins, the formation of an internal olefin on an oligomer end effectively removes reactivity from that end. The possible hydrogenation of the olefin can also contribute to the limiting of polymer size. Hydrogenation would also lead to deactivation of one end of the growing polymer.

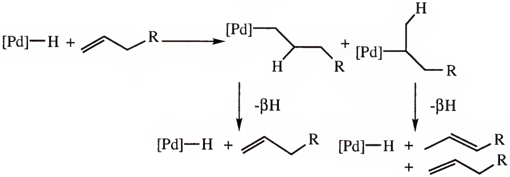


Figure 3.14 Mechanism for olefin isomerization.

A potential limitation to polymer size is due to errors in the stoichiometric ratio of diene to diol. For a successful polymerization, and exact 1:1 ratio of diene to diol is needed. As stated earlier, if one monomer is in excess of the other, polymer size is greatly diminished. The errors in stoichiometric ratio occur from experimental difficulty in the measurement of diene and diol. Attempts to make standard solutions of dienes and diol for the purpose of reducing the error associated in their measurements were unsuccessful. In making standards of the dienes and diols, a large dilution of the monomers occurs. This dilution, in itself, reduces molecular weight of polymers because of the nature of the step polymerization.

Polymer Synthesis Using Unsaturated Alcohols

Since the problem of an exact stoichiometric ratio limits the molecular weights of polymers made using dienes and diols as comonomers, an alternate monomer system was developed. In the carboalkoxylation reaction, the olefin functionality reacts with the alcohol functionality along with carbon monoxide. By incorporating the olefin and alcohol functionalities in one monomer, an α,ω-unsaturated alchohol, the use of two monomers is eliminated. Unsaturated alcohols have previously been used as substrates for carboalkoxylation to form small molecules, but not to form polymers (Tamaru 1987; Alper 1985; Norton 1979). Allylic alcohols and 4-butenols have been shown to cyclize into lactones in good yields (**Figure 3.15**).

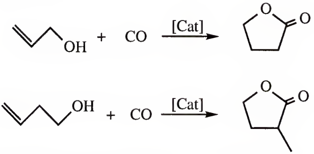


Figure 3.15 Cyclization of allyl alcohol and 4-butenol forming lactones.

To overcome the cyclization reaction, the alcohol and olefin functionalities have to be separated enough so one end of the monomer cannot easily react with the other end. Five and six membered rings are the most thermodynamically favored ring structures, and these rings are formed from three, four, and five carbon unsaturated alcohols. Therefore longer alkyl chain unsaturated alcohols must be used.

Synthesis of Poly(ω-undecylenoate)

In an inert atmosphere glove box, bis(triphenylphosphine) palladium dichloride and tin chloride hydrate were added to a glass vial equipped with a magnetic stirbar. To the vial was then added ω-undecylenyl alcohol. Acetone was then added to the vial and the vial was sealed with a cap with a hole to allow for changes in pressure. At this point the reaction mixture was red. The vial was then placed in the Parr high pressure reactor and the reactor was sealed. The reactor was removed from the glove box, pressurized to 1500 psi with carbon monoxide and heated to 75 °C. After 2 days pressure was released and the contents of the vial were poured into stirring hexanes forming a white precipitate (**Figure 3.16**).

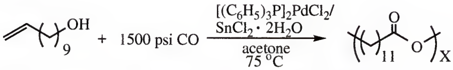


Figure 3.16 Formation of poly(ω-undecylenoate), **16**.

Poly(ω-undecylenoate), **16**, was a waxy white solid material. The M_W of the polymer was 2800 with a polydispersity of 1.7. Although the stoichiometric problems associated with two organic monomers are eliminated, the limitations to molecular weight observed in the reaction of dienes with diols and carbon monoxide also occur with ω-undecylenyl alcohol. The M_W is similar to those of the polymers formed from dienes, diols, and carbon monoxide. Again the polymer appears to be mostly linear with a triplet resonance in the ^1H NMR at δ 2.3 which corresponds to the methylene α to the carbonyl which integrates to an even number of protons. The amount of end groups of this polymer do not correspond to the amount expected relative to its molecular weight, probably due to a large degree of ring formation. The olefinic end is in much lower concentration compared to the alcohol as observed with the poly(alkylene dodecanedioate)s and the reasons for this are probably the same as with the poly(alkylene dodecanedioate)s. Hydrogenation and isomerization of the olefin endgroup reduces the amount of terminal olefin. This process may infact be the molecular weight limiting reaction in carboalkoxylation.

Although the molecular weights of these carboalkoxylation polymers are low, they can be increased. Heating the polymers to 150 °C under vacuum for 24 hours greatly increases their molecular weights (**Table 3.2**). Heating the polymers causes a transesterification reaction to take place (**Figure 3.17**). When this happens endgroups are displaced by other polymer chains. The vacuum removes the more volatile endgroups, helping the reaction to proceed. This is the same type of reaction employed to make high molecular weight PET. The molecular weights of the carboalkoxylation polymers undergo a variable amount of change. The loss of endgroups can be observed in both the ^{1}H and ^{13}C NMR spectra (**Figure 3.18, Figure 3.19**).

Table 3.2 Polymer characterization data.

Polymer	$M_w{}^a$	$M_w{}^b$	$M_w/M_n{}^b$	$T_m{}^b$
13	900	1100	1.2	42.9 °C
14	2000	7000	1.9	42.1 °C
15	1000	40000	2.0	48.0 °C
16	2800	27000	1.8	75.5 °C

a. Initial polymer.
b. Polymer after heating at 150 °C under vacuum for 24h.

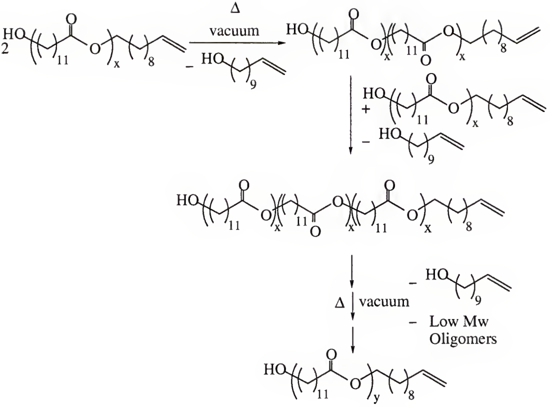


Figure 3.17 Increase of molecular weight of polymers by high temperature and low pressure condensation.

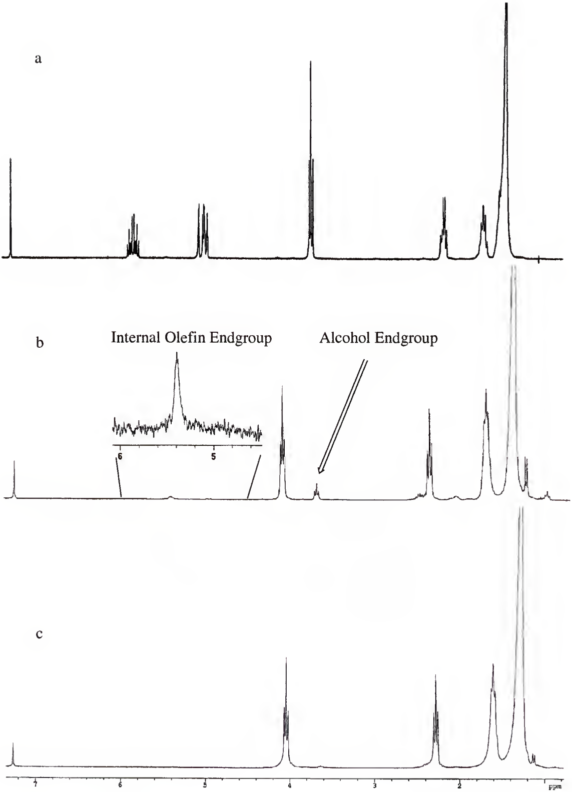


Figure 3.18 ^{1}H NMR (CDCl$_3$) spectra of a) undecylenyl alcohol, b) poly(ω-undecylenoate), c) poly(ω-undecylenoate) heated under vacuum.

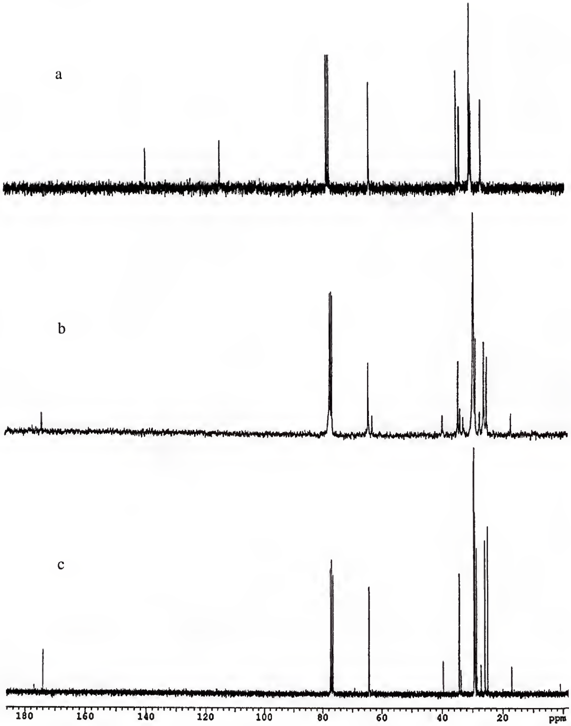


Figure 3.19 ^{13}C NMR ($CDCl_3$) spectra of a) undecylenyl alcohol, b) poly(ω-undecylenoate), c) poly(ω-undecylenoate) heated under vacuum.

Summary and Conclusions

Dienes and diols can be successfully copolymerized with carbon monoxide to produce poly(alkylene alkyloate)s. Each of these polymers is a white semisolid material. The molecular weights are low due to ring formation, stoichiometric errors, and competing reactions. The molecular weights can be increased by heating the polymers under vacuum. The higher molecular weight polymers are hard white plastics. ω-Unsaturated alcohols can also be copolymerized with carbon monoxide to produce poly(ω-alkyloate)s. Again the molecular weights are low due to ring formation and competing reactions, but can be increased by heating under vacuum.

CHAPTER 4

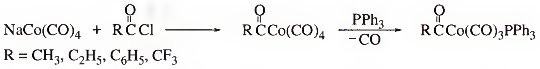
SYNTHESIS, STRUCTURE, AND REACTIVITY OF COBALT(III) COMPLEXES

Synthesis of Cobalt Complexes

The organometallic chemistry of cobalt has been relatively unexplored compared to other group 9 metals. The reason for this lack of study is due to the absence of facile routes to stable cobalt (I) or cobalt (III) complexes. Of the syntheses that exist, most rely on use of either $Co_2(CO)_8$, $CpCoL_n$, or $Co(acac)_3$ as starting materials.

A common precursor for cobalt (I) and (III) complexes is the reduced derivative of $Co_2(CO)_8$ in the form of its Co(-1) anion. The preparation of $NaCo(CO)_4$ does not involve the direct reduction of $Co_2(CO)_8$ with Na or Na/Hg as has been reported (Heiber 1958). Instead, $NaCo(CO)_4$ can be prepared in good yield from the reaction of $Co_2(CO)_8$ with NaOH in THF (Edgell 1970). $NaCo(CO)_4$ can then be used as a nucleophile to react with organic acid halides.

Heck (1962) has made a series of acylcobalt tetracarbonyl complexes from the reaction of $NaCo(CO)_4$ with acid halides (**Figure 4.1**). Simple acylcobalt tetracarbonyl compounds are thermally unstable as well as air sensitive. Substituting a phosphine on these complexes for one of the carbonyls creates the corresponding monophosphine compounds which are quite thermally stable.



$$NaCo(CO)_4 + R\overset{O}{\overset{\|}{C}}Cl \longrightarrow R\overset{O}{\overset{\|}{C}}Co(CO)_4 \xrightarrow[-CO]{PPh_3} R\overset{O}{\overset{\|}{C}}Co(CO)_3PPh_3$$

$R = CH_3, C_2H_5, C_6H_5, CF_3$

Figure 4.1 Preparation of acylcobalt complexes from $NaCo(CO)_4$ and acid halides.

Reaction of $NaCo(CO)_4$ with alkyl halides produces the corresponding alkylcobalt tetracarbonyl complexes. These too are thermally unstable and can be stabilized by addition of phosphine. Heck has reported that phosphine addition usually induces carbon monoxide insertion into the cobalt-alkyl bond, although some alkyl substituents do not undergo insertion (**Figure 4.2**). Unfortunately, in these systems the ligands around the metal are limited to CO and phosphines. This restriction severely hinders attempts to make new and different compounds starting from $NaCo(CO)_4$.

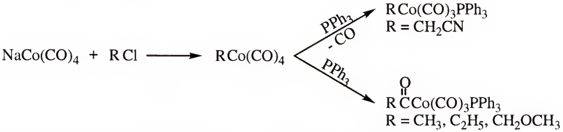


Figure 4.2 Preparation of acylcobalt and alkylcobalt complexes from $NaCo(CO)_4$ and alkyl halides.

Cyclopentadienyl cobalt complexes ($CpCoL_n$) constitute a large class of organocobalt compounds. A common precursor to these complexes is $CpCo(CO)_2$, which is usually prepared from $Co_2(CO)_8$ (Rausch 1980), or Cp_2Co (Jonas 1983 a,b). The cyclopentadienyl ring on $CpCo(CO)_2$ **17** can be modified in two ways. Friedel-Crafts acylation has been observed to occur on the Cp ring of **17** to produce acyl substituted Cp although this reaction only works for a limited number of acid halides (**Figure 4.3**) (Bönnemann 1985).

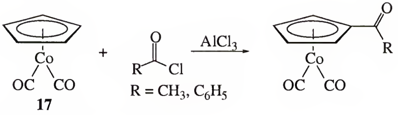


Figure 4.3 Friedel-Crafts acylation of **17**.

Alternatively, substituted Cp derivatives of **17** can be synthesized from $Co_2(CO)_8$. The reaction of a stoichiometric quantity of I_2 with $Co_2(CO)_8$ produces $ICo(CO)_4$ as a reactive intermediate. Treatment of this intermediate with the sodium salt of a substituted Cp produces the substituted Cp derivative of **17** in good yields (Rausch 1980). The direct reaction of $Co_2(CO)_8$ with a substituted cyclopentadiene also produces the substituted Cp derivative of **17** in good yields (Rausch 1970) (**Figure 4.4**). These methods have also been successfully employed to create indenyl and fluorenyl derivatives of **17**.

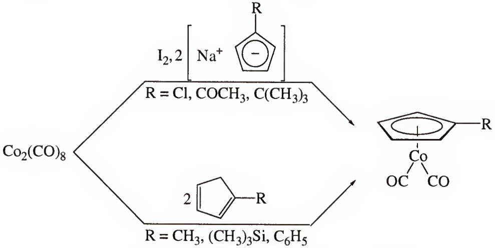


Figure 4.4 Synthesis of substituted Cp derivatives of **17** using $Co_2(CO)_8$.

The coordinated carbon monoxide ligands can be removed from $CpCo(CO)_2$, **17**, to produce new complexes. Irradiation of **17** and similar compounds in the presence of dienes such as 1,5 cyclooctadiene produces CpCoCOD complexes. Oxidation of **17** with I_2 creates the stable complex $[CpCoI_2]$ **18** which can be used as a versatile starting material (Brintzinger 1981). Reduction of **18** without a coordinating substrate produces cobaltocene. Reduction of **18** in the presence of dienes produces the corresponding CpCo(diene) complexes, while reduction of **18** in the presence of alkynes produce a variety of cobalt derivatives (**Figure 4.5**).

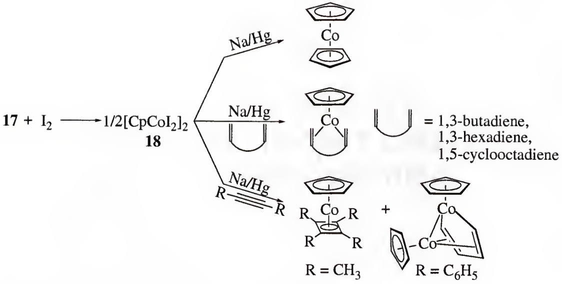


Figure 4.5 Reduction products of $[CpCoI_2]_2$, **18**.

Starting from either **17** or **18** a variety of cobalt complexes with interesting properties can be constructed. Brookhart (1991, 1985) has studied a series of cationic cobalt complexes containing the CpCo fragment (**Figure 4.6**). Protonation of a neutral cobalt-olefin complex forms the cationic species. Brookhart has shown these compounds to have activity toward α-olefin polymerizations. Unfortunately, study of cobalt complexes as olefin polymerization catalysts has been limited to Cp containing compounds because of a lack of synthetic pathways to stable, non-Cp organocobalt species.

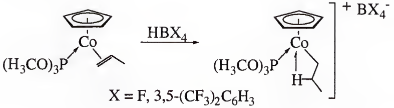


Figure 4.6 Generation of cationic cobalt catalyst for α-olefin polymerization.

A method for synthesizing non-Cp containing organocobalt complexes has been developed by Yamamoto (1976a, 1976b, 1975), and some of these are discussed in chapter 2. Reaction of $Co(acac)_3$ with $Al(CH_2CH_3)_2(OCH_2CH_3)$ in the presence of triphenylphosphine forms the compound $Co(C_2H_4)(acac)(PPh_3)_2$. Allowing this reaction to proceed in the presence of excess aluminum reagent leads to the compound $Co(C_2H_4)(PPh_3)_3$. Running this reaction in a nitrogen atmosphere leads to the complex $HCo(N_2)(PPh_3)_3$. Substitution of $Al(CH_3)_2(OCH_3)$ as the alkylating agent led only to $CH_3Co(PPh_3)_x$ (x = 2,3). Use of smaller, more electron donating phosphine ligands gave stable dialkyl cobalt (III) complexes of the general structure $CoR_2(acac)(PR_3)_2$, **19**. One phosphine can easily be displaced with pyridine, while both phosphines can be displaced by 2,2'-bipyridine. Complexes of the general structure **19** have been shown to readily insert carbon monoxide producing one equivalent of dialkyl ketone and $Co(acac)(CO)_2PR'_3$ (**Figure 4.7**).

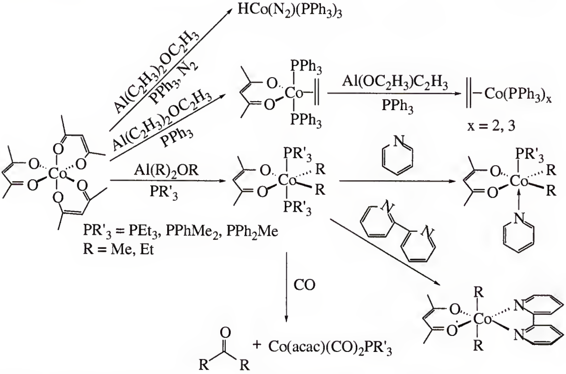
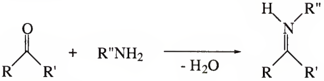


Figure 4.7 Cobalt complexes prepared from $Co(acac)_3$ and AlR_2OR.

Our interest in these complexes arises from the ability of the mixture $Co(acac)_3$ and AlR_3 to catalyze the copolymerization of propylene oxide and carbon monoxide to produce poly-β-hydroxybutyrate as outlined in Chapter 2. The lack of reactivity of **7**, **8**, and **9** toward catalyzing this polymerization led to the study of nonphosphine containing Co(acac) complexes. The methods of preparing Yamamoto's complexes do not allow for preparation of nonphosphine containing complexes. Fortunately, Bönnemann (1989) has described the preparation of several Co(acac) complexes without the need for phosphines. The activity, although limited, of **11** and **12** to catalyze the formation of poly-β-hydroxybutyrate has led to the study of new cobalt complexes containing β-diketonate-like ligands.

β-Diiminate Ligands

Acetylacetone contains two carbonyl functionalities which can easily be derivatized. Ketones and aldehydes undergo facile condensations with amines to make imines (**Figure 4.8**). Removal of water through azeotropic distillation or use of molecular sieves aids in formation of the imine. The use of primary amines containing substituents of variable steric and electronic effects allows for the creation of a wide array of imines.



R = alkyl, aryl
R' = H, alkyl, aryl
R" = alkyl, aryl

Figure 4.8 Preparation of imines from the condensation of ketones or aldehydes and amines.

Preparation of the β-diimines of acetylacetone proceeded in a two step synthesis described by Holm (1968) (**Figure 4.9**). In the first step, acetylacetone reacted with one equivalent of amine in refluxing ethanol. Concentration of the reaction mixture and subsequent cooling lead to formation of a crystalline eneamino ketone for most alkyl or aryl amines. Recrystallization of these products could be accomplished from diethyl ether or pentane and produced pure compounds in moderate yields. These β-ketoeneamines could be used themselves as ligands or could undergo further reactions to make β-diimines. The eneamino ketone reacted with one equivalent of amine hydrochloride in refluxing ethanol. Upon cooling, a crystalline β-diimine hydrochloride precipitated from solution. Neutralization with base followed by extraction with diethyl ether afforded the neutral β-diimine. Recrystallization of these β-diimines from diethyl ether or pentane produced crystalline compounds in variable yields. Both the eneamino ketones and the β-diimines are mildly hygroscopic and need to be stored in a desiccator if not to be used immediately.

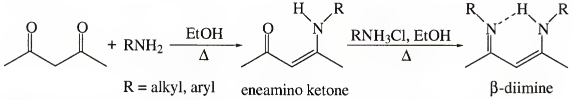
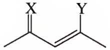
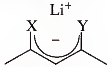


Figure 4.9 Syntheses of eneamino ketones and β-diimines of acetylacetone.

Deprotonation of the eneamino ketones proceeded smoothly. Addition of one equivalent of n-butyllithium to a room temperature pentane solution of an eneamino ketone caused immediate formation of a yellow precipitate. This air and moisture sensitive precipitate could be isolated by filtration to give the pure lithiate in good yield. Deprotonation of the β-diimines also proceeded smoothly. Addition of one equivalent of n-butyllithium to a room temperature pentane solution of a β-diimine caused an immediate color change to dark yellow often without formation of a precipitate. Removal of solvent *in vacuo* revealed a yellow air and moisture sensitive solid lithium β-diiminate in essentially quantitative yield (**Table 4.1**).

Table 4.1 Prepared enamido ketone, β-diimines and their lithiate salts.

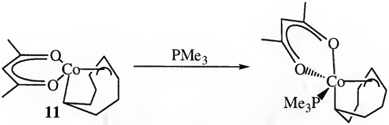




Enamino Ketone or β-Diimine		% Yield	Lithium Enamido Ketone or Lithium β-Diiminate		% Yield
X	Y		X	Y	
O	MeN	52.0	O	MeN	76.6
O	PhN	58.6	O	PhN	19.3
O	*p*-BrPhN	44.3	O	*p*-BrPhN	———
O	*p*-MeOPhN	38.5	O	*p*-MeOPhN	56.4
PhN	PhN	68.2	PhN	PhN	66.2
p-BrPhN	*p*-BrPhN	27.0	*p*-BrPhN	*p*-BrPhN	100
p-MeOPhN	*p*-MeOPhN	10.7	*p*-MeOPhN	*p*-MeOPhN	100
2,6-*i*PrPhN	2,6-*i*PrPhN	61.2	2,6-*i*PrPhN	2,6-*i*PrPhN	100

Synthesis and Characterization of Cobalt Complexes

Bönnemann (1989) synthesized a series of cobalt complexes containing the η^1, η^3-cyclooctenediyl moiety. $CpCoC_8H_{12}$ crystallized as a red solid, while $acacCoC_8H_{12}$, **11**, crystallized as a green solid. Exchanging acac for 1,1,1,5,5,5-hexafluoroacetylacetone produced a red compound. It has been reported that **11** reversibly coordinates THF which could be observed by the formation of a red solution upon addition of THF into a previously green pentane solution of **11**. Other ligands such as trimethylphosphine (PMe_3) could be coordinated to **11** (**Figure 4.10**). Addition of excess PMe_3 to a pentane solution of **11** immediately resulted in formation of a red solution. Removal of solvent *in vacuo* revealed a red solid which could be redissolved in pentane. Cooling the solution to -78 °C resulted in formation of brown red crystals. The ^1H NMR spectrum of the product showed a complete loss of the symmetry evident in **11**. This would be consistent with the formation of an octahedral complex by rotation of the acac ligand and coordination of PMe_3. This new molecule, **13**, has an arrangement of ligands with the PMe_3, allyl, and one oxygen of the acac ligand all lying in the same plane, while the other oxygen of the acac and the σ-bound carbon of the C_8 ring lie in axial positions 90 ° to this plane.



11

13

Figure 4.10 Coordination of PMe_3 to **11**.

Carbon monoxide and *t*-butyl isocyanide also coordinate to **11**, although decomposition of these complexes occurs after a short period of time. Coordination of CO to **11** produced an immediate color change to red. The ^1H NMR spectrum of this complex was similar to that of **13** lending evidence that CO is coordinating in a similar manner as PMe_3 (**Figure 4.11**). Coordination of CO is a reversible process for short periods of time. Removal of volatiles from the red mixture of CO and **11** produced a green solid identical to **11**. It is possible that insertion of CO or *t*-butyl isocyanide into the C_8 ring leads to formation of an unstable acyl species which then decomposes.

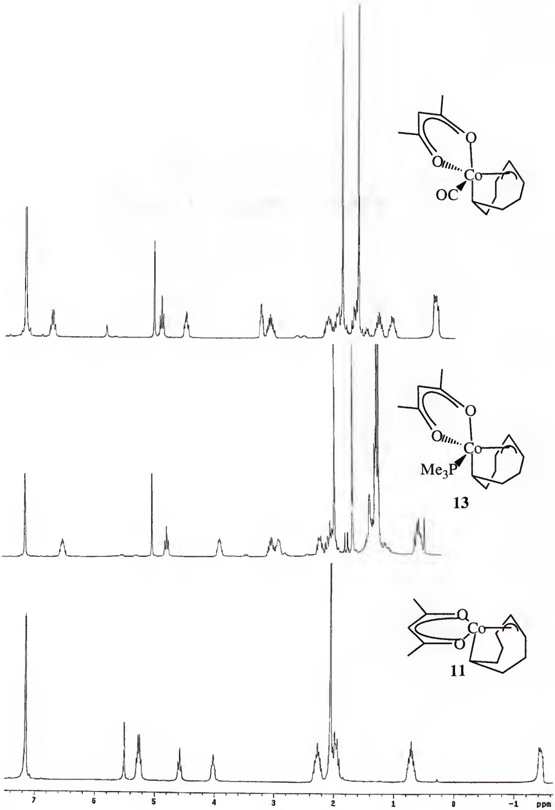
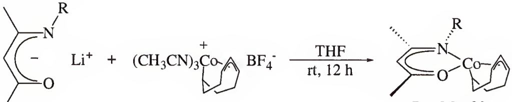


Figure 4.11 ^{1}H NMR spectra of ligand coordinated complexes of **12**.

Enamido Ketonate Cobalt Complexes

Several complexes containing the eneamido ketone ligands listed in table 4.1 were synthesized. A solution of one equivalent of lithium enamido ketonate was mixed with $[Co(CH_3CN)_3C_8H_{12}]BF_4$ in THF (**Figure 4.12**). Immediately, the solution changed from red to green. After stirring for 12 h, pentane was added, the solution was filtered, and solvent was removed *in vacuo*. The resulting green solid was extracted into pentane and the solution was cooled to -78 °C. Over the course of several days dark green crystals formed and were isolated.



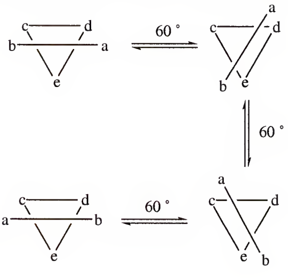
R = Me, **20**
Ph, **21**

Figure 4.12 Synthesis of enamido ketonate complexes of cobalt.

All of these complexes are soluble in most organic solvents although their stabilities in halogenated solvents are low. At room temperature, a methylene chloride solution of **20** decomposed over the course of an hour to produce paramagnetic material. The ^1H NMR spectra of these complexes showed a large amount of fluxional behavior. Compound **21** showed broadened peaks corresponding to the ortho protons on the phenyl ring and the terminal allyl protons as well as a pseudo symmetry in the C_8 ring due to fluxionality (**Figure 4.13**). Upon cooling to -80 °C, the fluxional process in this complex is slow on the NMR timescale. The low temperature spectrum contains inequivalent ortho protons on the phenyl ring due to one proton pointing toward the C_8 ring while the other points in the opposite direction. This spectrum can only occur if there is hindered rotation about the nitrogen-phenyl bond. This assignment is in agreement with the structure of **21** in the solid state (**Figure 4.14**). Simple hindered rotation of the phenyl ring does not explain why the C_8 ring is symmetrical at room temperature. The only way the C_8 ring can become symmetrical is if the enamido ketone ligand rotates allowing a time averaged C_8 ring to be observed in the ^1H NMR spectrum.

The rotation of the enamido ketone can be discussed using the turnstile mechanism for intramolecular ligand exchange (Ugi 1971) (**Scheme 4.1**). The turnstile mechanism has been used to explain intramolecular ligand exchange in other square pyramidal late transition metal complexes (Espinet 1997). This process can be viewed as rotation of ligands a and b (the enamido ketone ligand for **21**) around a common axis while ligands c,d, and e move little. A series of 60 ° rotations of the a-b group results in a molecule where a and b have exchanged places. Evidence for this process is seen in **13** which is essentially the trapped intermediate which occurs during the turnstile rotation of the ligands of **11**.

Scheme 4.1 Turnstile mechanism for intramolecular ligand exchange.



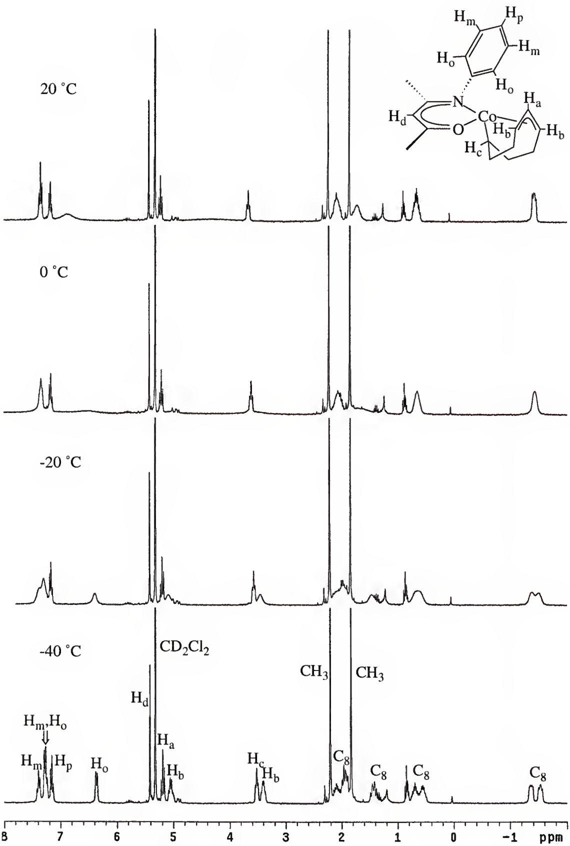


Figure 4.13 Variable temperature ^{1}H NMR spectra of **21**.

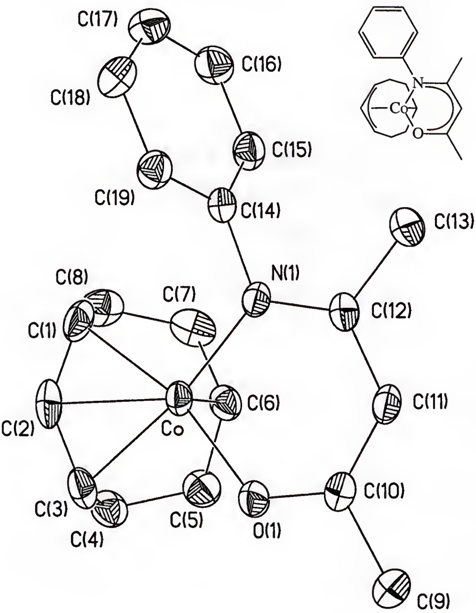


Figure 4.14 Molecular structure of $CH_3C(NPh)CHC(O)CH_3CoC_8H_{12}$, **21**. with 50% thermal ellipsoids and showing the atom numbering scheme. All hydrogen atoms are omitted for clarity.

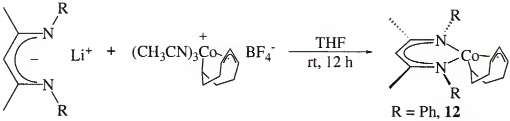
Table 4.2 Selected Bond Lengths (Å) and Angles (°) for **21**.

1	2	3	1-2	1-2-3
O1	Co	C3	1.9039(16)	92.43(9)
O1	Co	C2		125.25(10)
O1	Co	C1		165.45(9)
O1	Co	C6		95.21(9)
O1	Co	N1		94.40(7)
N1	Co	C1	1.9360(19)	99.71(9)
N1	Co	C3		171.42(9)
N1	Co	C6		98.90(9)
N1	C14	C19	1.439(3)	119.9(2)
C2	Co	N1	1.956(2)	131.17(10)
C6	Co	C1	1.981(3)	86.15(11)
C1	Co	C3	2.073(2)	73.20(10)
C3	Co	C6	2.099(2)	85.63(10)
C1	C2	C3	1.413(4)	124.2(2)
C3	C2	C1	1.402(4)	

Single crystals of **21** were grown by cooling a pentane solution of **21** to -78 °C for several days. Compound **21** has a slightly distorted square pyramidal geometry with the nitrogen and oxygen of the enamino ketonate and the terminal carbons of the allyl group lying in the same plane. The Co-C1 bond length of 2.073(2) Å is slightly longer than the Co-C3 bond length of 2.099(2) Å while the C1-C2 bond length of 1.413(4) Å is slightly longer than the C3-C2 bond length of 1.402(4) Å indicating an unsymmetrical allyl species. The steric congestion due to the C_8 ring being multidentate results in the phenyl ring being tilted perpendicular to the plane of atoms N1, Co, and C1. This tilt is manifested in a torsion angle of 75.2(2)° between the Co-N1 bond and the C14-C19 bond.

β-Diimidate Cobalt Complexes

Several complexes containing the β-diiminate ligands listed in table 4.1 were synthesized. A solution of one equivalent of lithium β-diimidate was mixed with $[Co(CH_3CN)_3C_8H_{12}]BF_4$ in THF (**Figure 4.15**). Immediately, the solution changed from red to green. After stirring for 12 h, pentane was added, the solution was filtered, and solvent was removed *in vacuo*. The resulting green solid was extracted into pentane and the solution was cooled to -78 °C. Over the course of several days dark green crystals formed and were isolated.



R = Ph, **12**
p-MeOPh, **22**

Figure 4.15 Synthesis of β-diimidate complexes of cobalt.

These complexes were soluble in most organic solvents except acetonitrile. Their stabilities in halogenated solvents were low as with the eneamido ketone complexes. The ^{1}H NMR spectra of these complexes also showed a large amount of fluxional behavior. Compound **12** showed broadened peaks similar to **21** corresponding to the ortho protons on the phenyl ring due to hindered rotation, but did not show any fluxional behavior for the allyl protons (**Figure 4.16**). The rotation of the aromatic ring can be slowed at low temperatures similarly to **21**. The X-ray crystal structure was similar to that of **21**, and showed the phenyl rings lying perpendicular to the equatorial plane of the molecule (**Figure 4.17**).

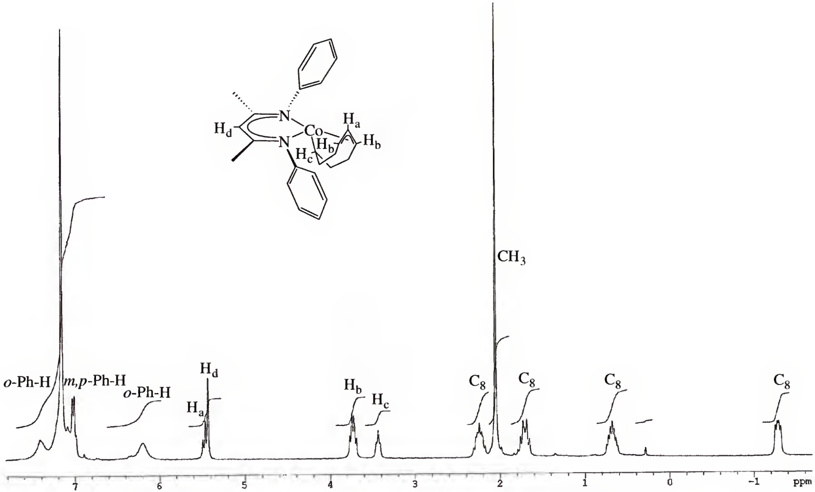


Figure 4.16 ^{1}H NMR spectrum of $CH_3C(NPh)CHC(NPh)CH_3CoC_8H_{12}$, **12**.

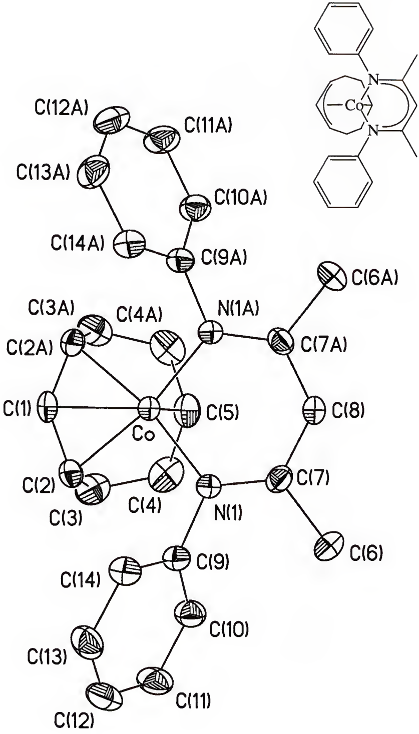


Figure 4.17 Molecular structure of $CH_3C(NPh)CHC(NPh)CH_3CoC_8H_{12}$, **12**. with 50% thermal ellipsoids and showing the atom numbering scheme. All hydrogen atoms are omitted for clarity.

Table 4.3 Selected Bond Lengths (Å) and Angles (°) for **12**.

1	2	3	1-2	1-2-3
N1	Co	N1A	1.935(2)	93.53(14)
N1	C9	C10	1.436(3)	122.6(3)
C1	Co	C5	1.965(4)	130.01(19)
C2	Co	C5	2.113(3)	85.36(15)
C5	Co	N1	1.969(4)	95.79(11)
C2	C1	C2A	1.413(4)	125.0(4)

Single crystals of **12** were grown by cooling a pentane solution of **12** to -78 °C for several days. Compound **12** has a slightly distorted square pyramidal geometry similar to **21**. The Co atom, C_1, C_5, and C_8 lie in a crystallographic mirror plane. Again as with **21**, the steric congestion due to the C_8 ring being multidentate resulted in both phenyl rings being tilted perpendicular to the plane of atoms N1, Co, and C2. This tilt is manifested in a torsion angle of 106.7(3) ° between the Co-N1 bond and the C9-C10 bond.

In the presence of carbon monoxide or isocyanide **12** immediately turned from green to red. Unfortunately, the formation of paramagnetic material made elucidation of the product difficult. No color change was observed upon addition of PMe_3 to a solution of **12**, and no coordination could be detected by ^1H NMR spectroscopy. Ideally, it would be helpful to remove the C_8 ring to make new complexes from **12**. Attempts to reduce **12** with H_2 also led to formation of paramagnetic material. Often protonation of an alkyl group is facile leading to a cationic metal species (Van Koten 1989). However, protonation of **12** with Brönsted acids in a mixture of acetonitrile and benzene led only to formation of $[(CH_3CN)_3CoC_8H_{12}]X$. It is possible that either the allyl carbons or the C5 carbon on the C_8 ring were too sterically crowded to easily be protonated while the C8 carbon of the β-diiminate was more easily accessible (**Figure 4.18**).

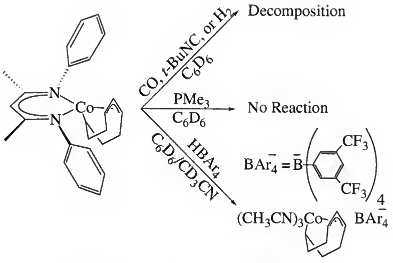
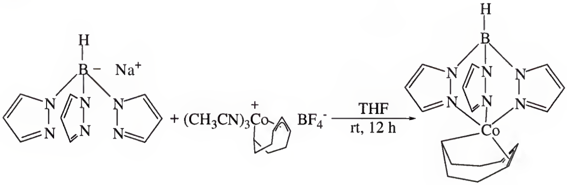


Figure 4.18 Attempted reactions with **12**.

In an effort to make a more stable cobalt complex containing the C_8 ring, the β-diiminate was exchanged with hydridotris(pyrazolyl)borate (Tp). Only a small number of Tp-cobalt complexes exist and most of those are in the +2 oxidation state. A solution of one equivalent of sodium Tp was mixed with $[Co(CH_3CN)_3C_8H_{12}]BF_4$ in THF (**Figure 4.19**). No color change was observed upon mixing. After stirring for 12 h, pentane was added, the mixture was filtered, and solvent was removed *in vacuo*. The resulting red-brown solid was extracted into pentane and the solution was cooled to -78 °C. Over the course of several days a red powder was isolated. Extraction of the red powder into pentane and cooling to -78 °C resulted in the formation of X-ray quality single crystals of **23**.



23

Figure 4.19 Synthesis of $TpCoC_8H_{12}$, **23**.

The ^1H NMR spectrum of **23** shows six pyrazole proton resonances (one is obscured by the solvent peak) indicating a plane of symmetry bisecting the molecule (**Figure 4.20**). The protons on the saturated carbons of the C_8 ring are shifted downfield compared to **21** and **12**, probably due to the tridentate nature of the Tp ligand versus the bidentate nature of the acac derivatives. No fluxionality of the Tp ligand can be observed in the ^1H NMR spectrum at room temperature.

The X-ray crystal structure of **23** agrees with the structure predicted from the ^1H NMR spectrum (**Figure 4.21**). This structure shows a non crystallographic plane of symmetry which bisects the molecule through the C6-Co-C2 plane. The pyrazole trans to C6 shows a longer bond distance to cobalt (2.1548(15) Å) than those of the other two pyrazole rings (1.9881(15) Å and 1.9984(14) Å). The allyl carbons show equal bond lengths to cobalt as was seen in **12**. Binding of the Tp ligand, except for the addition of a pyrazole ligand trans C6, is similar to that of the β-diiminate ligand in **12**.

Table 4.4 Selected Bond Lengths (Å) and Angles (°) for **23**.

1	2	3	1-2	1-2-3
N1	Co	C3	1.9881(15)	94.67(7)
N3	Co	C1	1.9984(14)	97.99(7)
N5	Co	C6	2.1548(15)	171.87(7)
C1	Co	N1	2.0962(18)	166.85(7)
C3	Co	N3	2.1015(18)	169.19(7)
C2	Co	N5	1.9864(17)	87.65(7)
C6	Co	N3	2.0190(17)	89.78(7)

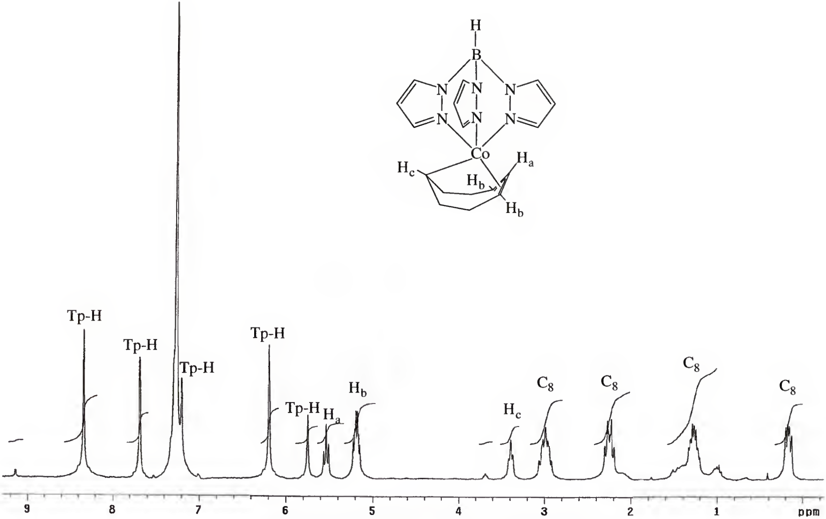


Figure 4.20 ^1H NMR spectrum of $TpCoC_8H_{12}$, **23**.

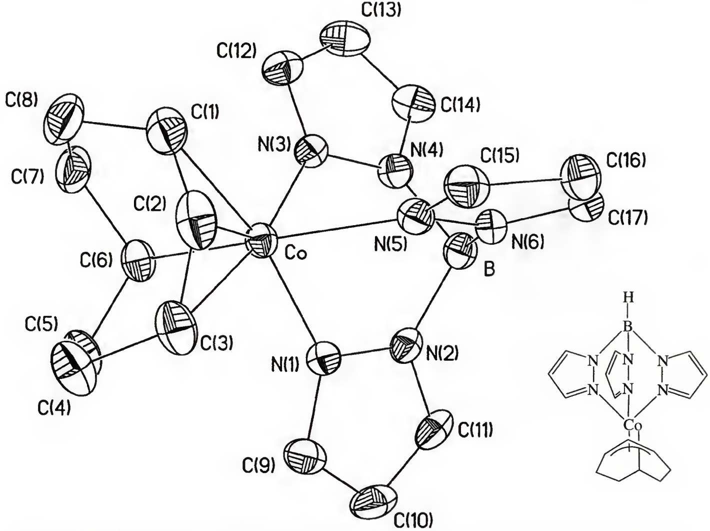


Figure 4.21 Molecular structure of $TpCoC_8H_{12}$, **23**. with 50% thermal ellipsoids and showing the atom numbering scheme. All hydrogen atoms are omitted for clarity.

Summary and Conclusions

Several new cobalt complexes of the type $XCoC_8H_{12}$, where X = eneamido ketone, β-diiminate, or Tp, were synthesized and characterized. These complexes show good stability in the solid state and moderate stability in solution. Asymmetric complexes containing bulky substituents on the ligand show fluxionality in the C_8 ring. Phenyl substituents on the ligand show hindered rotation. All of these complexes are able to catalyze the copolymerization of carbon monoxide and epoxides, but their activities are only marginal. One explanation for both the catalytic ability and low activity can be suggested by an isomerization of the C_8 ligand. Bönnemann (1989) has observed that CpCoη3,η1-C_8H_{12} when heated isomerizes to the η2,η2-cyclooctadienyl complex (**Figure 4.22**).

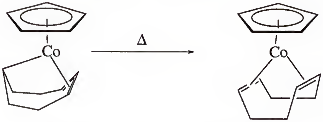


Figure 4.22 Isomerization of CpCoη3,η1-C_8H_{12} to CpCoη2,η2-C_8H_{12}.

This isomerization may be taking place with the cobalt complexes described herein. If this isomerization is slow or leads to a large amount of decomposition, the amount of active catalyst will be low leading to a small amount of polymer. To further explore this idea, η2,η2-cyclooctadienyl cobalt complexes need to be synthesized and tested, and their activities toward the polymerization determined.

CHAPTER 5
EXPERIMENTAL PROCEDURES

Materials and Methods

All procedures were performed using standard Schlenk techniques or in a nitrogen filled dry box, unless otherwise noted. Tetrahydrofuran (THF) was distilled from potassium benzophenone ketyl. Diethyl ether (Et_2O) was distilled from sodium benzophenone ketyl. Pentane and hexanes were distilled from sodium. Dichloromethane (CH_2Cl_2) and propylene oxide were distilled from calcium hydride. Chlorobenzene was dried over 4Å molecular sieves. Styrene oxide was dried by refluxing with benzene in a Dean Stark distilling receiver. All solvents were degassed and stored in sealable flasks containing 4Å molecular sieves after distillation. Epoxides were stored in flasks containing sodium sulfate after drying. Alcohols were fractionally distilled prior to use and stored over 4A molecular sieves. 1,9-Decadiene was distilled from sodium prior to use. All NMR solvents were degassed and stored over molecular sieves prior to use. The compounds $Pd(bipy)(Me)(NCMe)BAr_4$ (Brookhart 1992), $Cp_2Ti(NCMe)COMeBPh_4$ (Bochmann 1987), $Co(PPh_3)(CO)_2COMe$ (Heck 1962), $PPNFe(CO)_4COMe$ (Miller 1987), $LiFe(CO)_4COMe$ (Semmelhack 1983), $Na_2Fe(CO)_4 \cdot 1.5C_4H_8O_2$ (Finke 1979), $LiFe_2(CO)_6(PPh_2)COMe$ (Collman 1977), and $NaFe_2(CO)_8COMe$ (Collman 1977) were synthesized according to published procedures. The compounds $Pd(diphos)(Me)(NCMe)BAr_4$, $Pd(dppm)(Me)(NCMe)BAr_4$, $Pd(dmpe)(Me)(NCMe)BAr_4$ were prepared in a similar method to the published preparation of $Pd(bipy)(Me)(NCMe)BAr_4$. Glassware was oven dried prior to use. Propylene oxide, tin chloride hydrate, 1,9-decadiene, ω-undecylenyl alcohol, ethylene glycol, propane diol, butane diol, acetone, and hexanes were purchased from Aldrich Chemical Co. Carbon monoxide (CP grade) was purchased from Linde and used as received.

NMR spectra were collected either on a General Electric QE-300, Varian Gemini-300, or a Varian VXR-300 spectrometer. Chemical shifts were referenced in parts per million relative to the residual protons of the deuterated solvents and are reported relative to tetramethylsilane. IR were recorded on a Perkin Elmer 1200 series spectrometer from Nujol Mulls or KBr pellets prepared under a N_2 atmosphere. Mass spectra were obtained by the analytical services of the University of Florida. Thermal data were obtained with a DSC 2910 differential scanning calorimeter (DSC). DSC samples were analyzed over a temperature range of -120 °C to 40 °C with a scan rate of 10 °C/min and liquid nitrogen as the coolant. Molecular weight data were obtained using a Waters GPC with chloroform as a solvent and flow rate of 1 mL/min.

Polymerization Reactions

All polymerizations were carried out in glass vials inside one of two different reactors. The first is a 300 mL Parr high pressure reactor heated using a heating mantle. The second is a four chamber high pressure reactor designed by Dr. Steven Buelow of Los Alamos National Laboratories. This reactor is heated using a heating block fitted with an electronic temperature controller.

$(CH_2CH(CH_3)C(O)O)_x$ Synthesis a) Using a Cobalt Complex with Aluminum Cocatalyst b) Using a Well Defined Cobalt Complex

a) In an inert atmosphere glove box, $Co(acac)_3$ (0.102 g, 0.286 mmol) was placed in a glass vial equipped with a magnetic stirrer. Propylene oxide (2 mL, 1.66g, 0.029 mol) and then triethyl aluminum (0.04 mL, 0.033 g, 0.286 mmol) were placed into the vial. Immediately, the green solution changed to red with vigorous bubbling. A cap with a small hole in it was placed onto the vial. The vial was placed into the reactor and the reactor sealed. The reactor was then placed on a stirplate, pressurized with 1500 psi CO and heated to 105 °C. After stirring for 48 h, heating was stopped and pressure released. The vial was removed from the reactor and all volatiles removed *in vacuo* leaving a red oil. This is the same method used for all reactions using a cobalt catalyst with an aluminum cocatalyst.

b) In an inert atmosphere glove box, $C_8H_{12}CoC_8H_{13}$ (0.05 g, 0.181 mmol) was placed in a glass vial equipped with a magnetic stirrer. Propylene oxide (2 mL, 1.66g, 0.029 mol) was then added to the vial and a cap with a small hole in it was placed onto the vial. The vial was placed into the reactor and the reactor sealed. The reactor was then placed on a stirplate, pressurized 1500 psi with CO and heated to 105 °C. After stirring for 48 h, heating was stopped and pressure released. The vial was removed from the reactor and all volatiles removed *in vacuo* leaving a red oil. This polymer was made in the same manner using $acacCoC_8H_{12}$, and $(PhN)_2acacCoC_8H_{12}$ as catalysts.

^1H NMR (25 °C in $CDCl_3$): δ 1.28 (br s, 3H, CH_3), 2.50 (br d, 2H, CH_2), 5.25 (br s, 1H, CH). ^{13}C NMR (25 °C in $CDCl_3$) δ 19.8 (CH_3), 40.8 (CH), 67.6 (OCH_2), 169.2 (C=O). IR (NaCl): 1731 (s, C=O) cm^{-1}.

$\underline{((CH_2)_{10}C(O)OCH_2CH_2OC(O))_x}$

In an inert atmosphere glove box, $(PPh_3)_2PdCl_2$ (0.050 g, 0.071 mmol) and $SnCl_2{\cdot}2H_2O$ (0.080 g, 0.35 mmol) were added to a glass vial equipped with a magnetic stirbar. To the vial were then added decadiene (3.38 mL, 2.46 g, 0.018 mol) and ethylene glycol (0.99 mL, 1.11 g, 0.018 mol). Acetone (20 mL) was then added to the vial and the vial was sealed with a cap with a hole to allow for changes in pressure. At this point the reaction mixture was red. The vial was then placed in the reactor and the reactor was sealed. The reactor was removed from the glove box, placed on a stirplate, pressurized to 1500 psi with CO, and heated to 75 °C. After stirring for 24 h, pressure was released and the contents of the vial were poured into stirring hexanes forming a white semisolid precipitate.

^1H NMR (25 °C in $CDCl_3$) $\delta = 1.30$ (s, 12H, $C\underline{H}_2$), 1.61 (s, 4H, $COCH_2C\mathit{H}_2$), 2.35 (m, 4H, $CO\text{-}C\mathit{H}_2$), 4.30 (s,4H, $0\text{-}C\mathit{H}_2$). ^{13}C NMR (25 °C in $CDCl_3$) δ 24.62, 28.93, 29.10, 29.21, 33.92 ($\mathit{C}H_2$), 62.01 ($O\mathit{C}H_2$), 179.52 ($\mathit{C}=O$). IR (NaCl): 1735 cm^{-1} (s, C=O).

$((CH_2)_{10}C(O)OCH_2CH_2CH_2OC(O))_x$

In an inert atmosphere glove box, $(PPh_3)_2PdCl_2$ (0.050 g, 0.071 mmol) and $SnCl_2{\cdot}2H_2O$ (0.080 g, 0.35 mmol) were added to a glass vial equipped with a magnetic stirbar. To the vial were then added decadiene (3.38 mL, 2.46 g, 0.018 mol) and 1,3-propanediol (1.29 mL, 1.36 g, 0.018 mol). Acetone (20 mL) was then added to the vial and the vial was sealed with a cap with a hole to allow for changes in pressure. At this point the reaction mixture was red. The vial was then placed in the reactor and the reactor is sealed. The reactor was removed from the glove box, placed on a stirplate, pressurized to 1500 psi with CO, and heated to 75 °C. After stirring for 24 h, pressure was released and the contents of the vial were poured into stirring hexanes forming a white semisolid precipitate.

^1H NMR (25 °C in $CDCl_3$) $\delta = 1.27$(s, 12H, $C\mathit{H}_2$), 1.60 (s, 4H, $COCH_2\text{-}C\mathit{H}_2$), 1.98 (t, 2H, $OCH_2C\mathit{H}_2CH_2O$), 2.29 (t, 4H, $CO\text{-}C\mathit{H}_2$), 4.14 (t, 4H, $0\text{-}C\mathit{H}_2$). ^{13}C NMR (25 °C in $CDCl_3$) δ 24.90, 29.12, 29.20, 29.35, 34.22 ($\mathit{C}H_2$), 27.98 ($OCH_2\mathit{C}H_2CH_2O$), 60.82 ($O\mathit{C}H_2$), 173.79 ($\mathit{C}=O$). IR (NaCl): 1735 cm^{-1} (s, C=O).

$((CH_2)_{10}C(O)OCH_2CH_2CH_2CH_2OC(O))_x$

In an inert atmosphere glove box, $(PPh_3)_2PdCl_2$ (0.050 g, 0.071 mmol) and $SnCl_2{\cdot}2H_2O$ (0.080 g, 0.35 mmol) were added to a glass vial equipped with a magnetic stirbar. To the vial were then added decadiene (3.38 mL, 2.46 g, 0.018 mol) and 1,4-

butanediol (1.58 mL, 1.61 g, 0.018 mol). Acetone (20 mL) was then added to the vial and the vial was sealed with a cap with a hole to allow for changes in pressure. At this point the reaction mixture was red. The vial was then placed in the reactor and the reactor was sealed. The reactor was removed from the glove box, placed on a stirplate, pressurized to 1500 psi with CO, and heated to 75 °C. After stirring for 24 h, pressure was released and the contents of the vial were poured into stirring hexanes forming a white semisolid precipitate (3.40 g, 0.013 mol, 75 %).

^1H NMR (25 °C in $CDCl_3$) $\delta = 1.25$ (s, 12H, CH_2), 1.59 (m, 4H, $COCH_2$-CH_2), 1.67 (m, 4H, OCH_2CH_2), 2.27 (t, 4H, CO-CH_2), 4.07 (s, 4H, 0-CH_2). ^{13}C NMR (25 °C in $CDCl_3$) δ 25.06, 25.27, 29.09, 29.18, 29.20 (CH_2), 63.70 (OCH_2), 173.91 (C=O). IR (NaCl): 1735 cm^{-1} (s, C=O).

$((CH_2)_{11}C(O)O)_x$

In an inert atmosphere glove box, $(PPh_3)_2PdCl_2$ (0.050 g, 0.071 mmol) and $SnCl_2{\cdot}2H_2O$ (0.080 g, 0.35 mmol) were added to a glass vial equipped with a magnetic stirbar. To the vial was then added ω-undecylenyl alcohol (2.43 g, 0.014 mol). Acetone (25 mL) was then added to the vial and the vial was sealed with a cap with a hole to allow for changes in pressure. At this point the reaction mixture was red. The vial was then placed in the reactor and the reactor is sealed. The reactor is removed from the glove box, placed on a stirplate, pressurized to 1500psi with CO, and heated to 75 °C. After 24 h, pressure was released and the contents of the vial were poured into stirring hexanes forming a white solid precipitate (2.40 g, 0.012 mol, 85 %).

^1H NMR (25 °C in $CDCl_3$) $\delta = 1.27$ (s, 14H, CH_2), 1.60 (m, 4H, $C(O)CH_2$-CH_2), 2.28 (t, 2H, $C(O)CH_2$), 4.05 (t, 2H, O-CH_2). ^{13}C NMR (25 °C in $CDCl_3$) δ 24.99, 25.92, 28.64, 29.15, 29.26, 29.42, 29.49, 34.37 (CH_2), 64.36 (OCH_2), 173.94 (C=O). IR (NaCl): 1735 cm^{-1} (s, C=O).

$CH_3OC(O)CH_2CH(CH_3)OH$

In an inert atmosphere glove box, $C_8H_{12}CoC_8H_{13}$ (0.138 g, 0.500 mmol) was placed in a glass vial equipped with a magnetic stirrer. Propylene oxide (7.00 mL, 5.81 g, 0.100 mol) and methanol (4.05 mL, 3.21 g, 0.100 mol) were then added to the vial and a cap with a small hole in it was placed onto the vial. The vial was placed into the reactor and the reactor sealed. The reactor was then placed on a stirplate, pressurized 1600 psi with CO and heated to 105 °C. After stirring for 48 h, heating was stopped and pressure released. The vial was removed from the reactor and its contents were distilled, producing 4.108 g methylhydroxybutyrate (0.0348 mol, 34.8 %).

^1H NMR (25 °C in $CDCl_3$) δ 1.22 (d, 3H, CH_3), 2.49 (d, 2H, CH_2), 3.70 (s, 3H, OCH_3), 4.20 (m, 1H, CH).

$LiCH_3C(NCH_3)CHC(O)CH_3$

To a 0 °C stirring solution of $CH_3C(NHCH_3)CHC(O)CH_3$ (0.91 g, 8.04 mmol) in 30 mL pentane was added n-butyllithium (2.5 M, 3.22 mL, 8.04 mmol). The solution turned yellow without any visible precipitate. The solution was allowed to warm to room temperature and stirred for 1 h. Solvent was removed *in vacuo* leaving a yellow powder (0.85 g, 6.23 mmol, 77.5%).

^1H NMR (25 °C in DMSO-d^6) δ 1.58 (s, 3H, CH_3), 1.60 (s, 3H, CH_3), 2.81 (s, 3H, NCH_3), 4.37 (s, 1H, CH).

$LiCH_3C(NPh)CHC(O)CH_3$

To a 0 °C stirring solution of $CH_3C(NHPh)CHC(O)CH_3$ (1.06 g, 6.02 mmol) in 30 mL pentane was added n-butyllithium (1.6M, 4.14 mL, 6.62 mmol). Immediately, a white precipitate began to form. The solution was allowed to warm to room temperature, and was stirred for 1 h. The white solid was filtered, washed twice with pentane, then dried *in vacuo* yielding a white powder (0.26 g, 1.45 mmol, 24.0 %).

^{1}H NMR (25 °C in DMSO-d^6) δ 1.59 (s, 3H, C*H*$_3$), 1.69 (s, 3H, C*H*$_3$), 4.57 (s, 1H, C*H*), 6.71 (d, 2H, o-Ph), 6.85 (t, 1H, p-Ph), 7.16 (t, 2H, m-Ph).

Li(o-(PhNCH)(O)C_6H_4)

To a 0 °C stirring solution of o-(PhNCH)(OH)C_6H_4 (1.64 g, 8.32 mmol) in 30 mL pentane was added n-butyllithium (2.5 M, 3.66 mL, 9.15 mmol). Immediately, a yellow precipitate began to form. The solution was allowed to warm to room temperature, and was stirred for 1 h. The yellow solid was filtered, washed twice with pentane, then dried *in vacuo* yielding a yellow powder (1.515 g, 7.46 mmol, 89.6 %).

$LiCH_3C(p\text{-}OCH_3PhN)CHC(O)CH_3$

To a 0 °C stirring solution of $CH_3C(p\text{-}OCH_3PhNH)CHC(O)CH_3$ (1.41 g, 6.87 mmol) in 30 mL pentane was added n-butyllithium (2.5 M, 3.02 mL, 7.56 mmol). Immediately, a yellow precipitate began to form. The solution was allowed to warm to room temperature, and was stirred for 1 h. The yellow solid was filtered, washed twice with pentane, then dried *in vacuo* yielding a yellow powder (0.818 g, 3.87 mmol, 56.3 %).

^{1}H NMR (25 °C in DMSO-d^6) δ 1.58 (s, 3H, C*H*$_3$), 1.68 (s, 3H, C*H*$_3$), 3.68 (s, 3H, OC*H*$_3$), 4.55 (s, 1H, C*H*), 6.64 (d, 2H, Ph), 6.77 (d, 2H, Ph), 7.16 (t, 2H, m-Ph).

$LiCH_3C(NPh)CHC(NPh)CH_3$

To a 0 °C stirring solution of $CH_3C(NHPh)CHC(NPh)CH_3$ (0.315 g, 1.26 mmol) in 30 mL pentane was added n-butyllithium (2.5 M, 0.554 mL, 1.38 mmol). Immediately, a white precipitate began to form. The solution was allowed to warm to room temperature

and stirred for 1 h. The yellow solid was filtered, washed twice with pentane, then dried *in vacuo* yielding a white powder (0.234 g, 0.913 mmol, 66.2 %).
^{1}H NMR (25 °C in DMSO-d^6) δ 1.73 (s, 6H, C*H*$_3$), 4.29 (s, 1H, C*H*), 6.78 (m, 6H, *o,p*-Ph), 7.13 (t, 4H, *m*-Ph).

$\mathrm{LiCH_3C(p\text{-}OCH_3PhN)CHC(p\text{-}OCH_3PhN)CH_3}$

To a 0 °C stirring solution of $\mathrm{CH_3C(p\text{-}OCH_3PhNH)CHC(p\text{-}OCH_3PhN)CH_3}$ (0.44 g, 1.36 mmol) in 30 mL pentane was added n-butyllithium (2.5 M, 0.60 mL, 1.49 mmol). Immediately, a yellow precipitate began to form. The solution was allowed to warm to room temperature, and was stirred for 1 h. The yellow solid was filtered, washed twice with pentane, then dried *in vacuo* yielding a yellow powder (0.449 g, 1.36 mmol, 100 %).
^{1}H NMR (25 °C in DMSO-d^6) δ 1.68 (s, 6H, C*H*$_3$), 3.67 (s, 6H, OC*H*$_3$), 4.20 (s, 1H, C*H*), 6.70 (dd, 4H, Ph).

$\mathrm{CH_3C(NCH_3)CHC(O)CH_3CoC_8H_{12}}$, **20.**

A room temperature solution of $\mathrm{[Co(CH_3CN)_3C_8H_{12}]BF_4}$ (0.200 g, 0.530 mmol) in 20 mL THF was added to solid $\mathrm{LiCH_3C(NCH_3)CHC(O)CH_3}$ (0.063 g, 0.530 mmol). Immediately the solution turned from red to green. The solution was stirred for 2 h, then solvent was removed *in vacuo* leaving a green solid. The solid was extracted into pentane and the pentane solution was cooled to -78 °C, yielding **20** as green crystals (0.046 g, 0.165 mmol, 31.1 %).
^{1}H NMR (25 °C in C_6D_6) δ = -1.17 (m, 2H, CH*H*), 0.90 (m, 2H, CH*H*), 1.79 (s, 3H, C*H*$_3$), 1.98 (m, 3H, CH*H*), 2.27 (s, 3H, C*H*$_3$), 2.48 (br, 1H, CH*H*), 3.77 (t, 1H, CoC*H*), 3.80 (s, 3H, NC*H*$_3$), 4.20 (br, 1H, C*H*CHCH), 5.11 (t, 1H CHC*H*CH), 5.27 (s, 1H, CC*H*C), 5.57 (br, 1H, C*H*CHCH). ^{13}C NMR (25 °C in C_6D_6) δ = 23.08, 25.49,

25.92, 26.97, 39.36, 42.11, 43.32, 50.05, 64.38, 78.31, 98.52, 104.06, 168.35, 177.81.

$CH_3C(NPh)CHC(O)CH_3CoC_8H_{12}$, **21**.

A room temperature solution of $[Co(CH_3CN)_3C_8H_{12}]BF_4$ (0.200 g, 0.530 mmol) in 20 mL THF was added to solid $LiCH_3C(NPh)CHC(O)CH_3$ (0.106 g, 0.583 mmol). Immediately the solution turned from red to green. The solution was stirred for 2 h, then solvent was removed *in vacuo* leaving a green solid. The solid was extracted with pentane and the pentane solution was cooled to -78 °C, yielding **21** as dark green crystals (0.087 g, 0.225 mmol, 48.1 %).

^1H NMR (70 °C in C_6D_6) δ = -1.39 (m, 2H, CH*H*), 0.70 (m, 2H, CH*H*), 1.75 (s, 3H, CH_3), 1.78 (m, 2H, CH*H*), 2.28 (m, 2H, CH*H*), 2.30 (s, 3H, CH_3), 3.95 (t, 1H, CoC*H*), 4.60 (br, 2H, C*H*CHC*H*), 5.15 (t, 1H CHC*H*CH), 5.40 (s, 1H, CC*H*C), 6.70 (d, 2H, o-Ph), 6.95 (t, 1H, p-Ph), 7.09 (t, 2H, m-Ph).

o-$(PhNCH)(O)C_6H_4CoC_8H_{12}$, **26**.

A room temperature stirring solution of $[Co(CH_3CN)_3C_8H_{12}]BF_4$ (0.046 g, 0.123 mmol) in 20 mL THF was added to solid Li(*o*-$(PhNCH)(O)C_6H_4$) (0.025 g, 0.123 mmol). Immediately the solution turned from red to green. The solution was stirred for 2 h, then solvent was removed *in vacuo* leaving a green solid. The solid was extracted with pentane and the pentane solution was cooled to -78 °C, yielding **26** as yellow-green crystals (0.012 g, 0.033 mmol, 27.1 %).

^1H NMR (60 °C in C_6D_6) δ = -1.61 (m, 2H, CH*H*), 0.72 (m, 2H, CH*H*), 1.74 (m, 2H, CH*H*), 2.07 (m, 2H, CH*H*), 3.50 (t, 1H, CoC*H*), 4.89 (br, 2H, C*H*CHC*H*), 5.16 (t, 1H CHC*H*CH), (6.63 (br), 6.79 (d), 7.02 (t), 7.11 (m), 7.33 (t), 7.65 (br) all corresponding to phenyl protons), 8.38 (s, 1H, C*H*N).

$CH_3C(p\text{-}BrPhN)CHC(O)CH_3CoC_8H_{12}$, **24.**

To a room temperature stirring solution of $CH_3C(p\text{-}BrPhNH)CHC(O)CH_3$ (0.134 g, 0.530 mmol) in 20 mL THF was added n-butyllithium (2.5 M, 0.21 g, 0.530 mmol). The solution turned darker yellow and was stirred for 30 min. This solution was added to solid $[Co(CH_3CN)_3C_8H_{12}]BF_4$ (0.200 g, 0.530 mmol). Immediately the solution turned from red to green. The solution was stirred for 2 h, then solvent was removed *in vacuo* leaving a green solid. The solid was extracted with pentane and the pentane solution was cooled to -78 °C, yielding **24** as green crystals which turned yellow under vacuum. The product displayed no signal in the ^1H NMR.

$CH_3C(p\text{-}OCH_3PhN)CHC(O)CH_3CoC_8H_{12}$, **25.**

A room temperature solution of $[Co(CH_3CN)_3C_8H_{12}]BF_4$ (0.200 g, 0.530 mmol) in 20 mL THF was added to solid $LiCH_3C(p\text{-}OCH_3PhN)CHC(O)CH_3$ (0.112 g, 0.530 mmol). Immediately the solution turned from red to green. The solution was stirred for 2 h, then solvent was removed *in vacuo* leaving a green solid. The solid was extracted with pentane and the pentane solution was cooled to -78 °C, yielding **25** as dark green crystals (0.039 g, 0.105 mmol, 19.8 %).

^1H NMR (60 °C in C_6D_6) δ = -1.32 (m, 2H, CH*H*), 0.74 (m, 2H, CH*H*), 1.78 (s, 3H, CH_3), 1.80 (m, 2H, CH*H*), 2.26 (m, 2H, CH*H*), 2.32 (s, 3H, CH_3), 3.40 (s, 3H, OCH_3), 3.96 (t, 1H, CoC*H*), 4.66 (br, 2H, C*H*CHC*H*), 5.19 (t, 1H CHC*H*CH), 5.43 (s, 1H, CC*H*C), 6.62 (d, 2H, *o*-Ph), 6.74 (d, 2H, *m*-Ph).

$CH_3C(NPh)CHC(NPh)CH_3CoC_8H_{12}$, **12.**

A room temperature solution of $[Co(CH_3CN)_3C_8H_{12}]BF_4$ (0.449 g, 1.19 mmol) in 20 mL acetonitrile was added to solid $LiCH_3C(NPh)CHC(NPh)CH_3$ (0.305 g, 1.19 mmol). Immediately the solution turned from red to green. Over the course of 5 minutes small green crystals formed. The mixture was stirred for 30 min, then filtered leaving a green crystaline solid. The solid was dissolved into pentane and the pentane solution was cooled to -78^{o}C, yielding **12** as dark green crystals (0.283 g, 0.795 mmol, 57.1 %).

^{1}H NMR (25 °C in C_6D_6) δ = -1.26 (m, 2H, CH*H*), 0.70 (m, 2H, CH*H*), 1.70 (m, 2H, CH*H*), 2.05 (s, 6H, CH_3), 2.25 (m, 2H, CH*H*), 3.45 (t, 1H, CoC*H*), 3.70 (m, 2H, C*H*CHC*H*), 5.40 (s, 1H, CC*H*C), 5.45 (t, 1H CHC*H*CH), 6.18 (br s, 2H, half *o*-Ph protons), 7.20 (m, 8H, Ph).

Elemental analysis calculated for $C_{25}H_{29}N_2Co$: C, 72.10; H, 7.01; N, 6.72.

Found: C, 71.84; H, 7.36; N, 6.75.

CH_3C(*p*-OCH_3PhN)CHC(*p*-OCH_3PhN)$CH_3CoC_8H_{12}$, **22.**

A room temperature solution of [Co(CH_3CN)$_3$$C_8H_{12}$]$BF_4$ (0.200 g, 0.530 mmol) in 20 mL THF was added to solid LiCH_3C(*p*-OCH_3PhN)CHC(*p*-OCH_3PhN)CH_3 (0.175 g, 0.530 mmol). Immediately the solution turns from red to green. The solution was stirred for 30 min, then solvent was removed *in vacuo* leaving a green solid. The solid was extracted with toluene and solvent was removed *in vacuo* leaving a green solid. The solid was dissolved into pentane and the pentane solution was cooled to -78 °C, yielding **22** as green fluffy crystals (0.133 g, 0.280 mmol, 52.7 %).

^{1}H NMR (25 °C in C_6D_6) δ = -1.16 (m, 2H, CH*H*), 0.76 (m, 2H, CH*H*), 1.78 (m, 2H, CH*H*), 2.11 (s, 6H, CH_3), 2.29 (m, 2H, CH*H*), 3.37 (s, 6H, OC*H*$_3$), 3.47 (t, 1H, CoC*H*), 3.85 (m, 2H, C*H*CHC*H*), 5.48 (s, 1H, CC*H*C), 5.60 (t, 1H CHC*H*CH), 6.19, 6.70, 6.84, 7.32 (each as d, 2H each, Ph).

$TpCoC_8H_{12}$, **23.**

A room temperature solution of $[Co(CH_3CN)_3C_8H_{12}]BF_4$ (0.300 g, 0.796 mmol) in 20 mL THF was added to solid KTp (0.201 g, 0.796 mmol). The red solution was stirred for 2 h, then solvent was removed *in vacuo* leaving a light brown solid. The solid was extracted with pentane and the pentane solution was cooled to -78 °C, yielding **23** as red crystals (0.117 g, 0.306 mmol, 38.5 %).

^1H NMR (25 °C in $CDCl_3$) δ = 0.16 (m, 2H, CH*H*), 1.29 (m, 2H, CH*H*), 2.26 (m, 2H, CH*H*), 3.39 (t, 1H, CoC*H*), 5.18 (m, 2H, *C*HCHC*H*), 5.54 (t, 1H CHC*H*CH), 6.19, 7.69, 8.33 (s, 2H each, Tp ring protons, 3,5-positions), 5.75, 7.20, 7.29 (s, 1H each, Tp ring protons, 4-positions).

$CH_3C(O)CHC(O)CH_3Co(P(CH_3)_3)C_8H_{12}$, **13.**

To a room temperature solution of $CH_3C(O)CHC(O)CH_3CoC_8H_{12}$ (0.050 g, 0.118 mmol) in 10 mL of pentane was added $P(CH_3)_3$ (0.194 mL, 0.143 g, 0.188 mmol). Immediately the solution turned from dark green to deep red. The solution was stirred for 30 min, then solvent was removed *in vacuo* leaving a red solid. The red solid was redissolved in 20 mL of pentane, filtered, then concentrated to ~2 mL. After sitting at -78 °C for 3 days red-brown crystals formed and were collected (0.034 g, 0.099 mmol, 52.8 %).

^1H NMR (25 °C in $CDCl_3$) δ = 0.40 (m, 2H, CH*H*), 1.09 (d, 9H, $P(CH_3)_3$), 1.23 (m, 2H, CH*H*), 1.84 (s, 3H, CH_3), 1.84 (s, 3H, CH_3), 1.91 (m, 2H, CH*H*), 2.81 (br, 1H, CoC*H*), 2.94 (m, 1H, CH*H*), 3.82 (m, 1H, C*H*CHCH), 4.75 (t, 1H CHC*H*CH), 4.99 (s, 1H, CC*H*C), 6.53 (m, 1H, CHCHC*H*). ^{13}C NMR (25 °C in C_6D_6) δ = 14.43 (d), 25.30, 28.10, 28.85, 30.19, 36.80, 40.95, 45.40 (d), 58.58, 91.23 (d), 97.57, 112.74, 186.19, 188.77.

APPENDIX

TABLES OF CRYSTALLOGRAPHIC DATA

Crystallographic Data for $CH_3C(NPh)CHC(O)CH_3CoC_8H_{12}$, **21.**

Table A1.1. Crystallographic Data and Structure Refinement

Empirical formula	C19 H24 Co N O	
Formula weight	341.32	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.7572(6) Å	α= 88.3680(10)°.
	b = 9.2057(7) Å	β= 73.5540(10)°.
	c = 11.8393(9) Å	γ = 66.9380(10)°.
Volume	838.55(11) Å^3	
Z	2	
Density (calculated)	1.352 Mg/m^3	
Absorption coefficient	1.025 mm^{-1}	
F(000)	360	
Crystal size	0.09 x 0.10 x 0.16 mm^3	
Theta range for data collection	1.80 to 27.50°.	
Index ranges	$-11 \leq h \leq 11$, $-11 \leq k \leq 11$, $-15 \leq l \leq 14$	
Reflections collected	6007	
Independent reflections	3765 [R(int) = 0.0349]	
Completeness to theta = 27.50°	97.7 %	
Absorption correction	Integration	
Max. and min. transmission	0.915 and 0.872	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3765 / 0 / 199	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0386, wR2 = 0.1024 [3086]	
R indices (all data)	R1 = 0.0512, wR2 = 0.1082	
Largest diff. peak and hole	0.535 and -0.444 e.Å^{-3}	

Table A1.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **21**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
Co	3463(1)	1478(1)	1628(1)	22(1)
C1	1481(3)	711(3)	2310(3)	34(1)
C2	1562(3)	1280(3)	1183(2)	33(1)
C3	1428(3)	2817(3)	939(2)	31(1)
C4	280(3)	4337(3)	1747(2)	34(1)
C5	1290(4)	4644(3)	2510(2)	37(1)
C6	2266(3)	3128(3)	2985(2)	30(1)
C7	1181(4)	2544(4)	3966(2)	40(1)
C8	297(4)	1666(4)	3477(3)	43(1)
O1	4923(2)	2463(2)	759(1)	28(1)
N1	5235(2)	-15(2)	2247(2)	23(1)
C9	7274(3)	3248(3)	120(2)	33(1)
C10	6403(3)	2291(3)	882(2)	25(1)
C11	7229(3)	1258(3)	1596(2)	26(1)
C12	6736(3)	82(3)	2187(2)	24(1)
C13	8056(3)	-1120(3)	2696(2)	32(1)
C14	4921(3)	-1311(3)	2825(2)	24(1)
C15	4420(3)	-1271(3)	4052(2)	30(1)
C16	4049(4)	-2494(3)	4606(2)	35(1)
C17	4159(4)	-3753(3)	3947(3)	39(1)
C18	4665(4)	-3807(3)	2722(2)	35(1)
C19	5046(3)	-2590(3)	2157(2)	27(1)

Table A1.3. Bond lengths [Å] and angles [°] for **21**.

Co-O1	1.9039(16)
Co-N1	1.9360(19)
Co-C2	1.956(2)
Co-C6	1.981(3)
Co-C1	2.073(2)
Co-C3	2.099(2)
C1-C2	1.413(4)
C1-C8	1.517(4)
C1-H1A	0.9800
C2-C3	1.402(4)
C2-H2A	0.9800
C3-C4	1.522(4)
C3-H3A	0.9800
C4-C5	1.529(4)
C4-H4A	0.9700
C4-H4B	0.9700
C5-C6	1.512(3)
C5-H5A	0.9700
C5-H5B	0.9700
C6-C7	1.510(4)
C6-H6A	0.9800
C7-C8	1.535(4)
C7-H7A	0.9700
C7-H7B	0.9700
C8-H8A	0.9700
C8-H8B	0.9700
O1-C10	1.293(3)
N1-C12	1.334(3)
N1-C14	1.439(3)
C9-C10	1.505(3)
C9-H9A	0.9600
C9-H9B	0.9600
C9-H9C	0.9600
C10-C11	1.380(3)
C11-C12	1.414(3)
C11-H11A	0.9300
C12-C13	1.510(3)
C13-H13A	0.9600
C13-H13B	0.9600
C13-H13C	0.9600
C14-C19	1.388(3)
C14-C15	1.390(3)
C15-C16	1.388(4)
C15-H15A	0.9300
C16-C17	1.373(4)
C16-H16A	0.9300
C17-C18	1.386(4)
C17-H17A	0.9300
C18-C19	1.392(3)
C18-H18A	0.9300
C19-H19A	0.9300

O1-Co-N1	94.40(7)
O1-Co-C2	125.25(10)
N1-Co-C2	131.17(10)
O1-Co-C6	95.21(9)
N1-Co-C6	98.90(9)
C2-Co-C6	103.81(11)
O1-Co-C1	165.45(9)
N1-Co-C1	99.71(9)
C2-Co-C1	40.92(11)
C6-Co-C1	86.15(11)
O1-Co-C3	92.43(9)
N1-Co-C3	171.42(9)
C2-Co-C3	40.27(11)
C6-Co-C3	85.63(10)
C1-Co-C3	73.20(10)
C2-C1-C8	125.3(2)
C2-C1-Co	65.09(14)
C8-C1-Co	109.70(18)
C2-C1-H1A	115.2
C8-C1-H1A	115.2
Co-C1-H1A	115.2
C3-C2-C1	124.2(2)
C3-C2-Co	75.37(14)
C1-C2-Co	73.99(14)
C3-C2-H2A	117.7
C1-C2-H2A	117.7
Co-C2-H2A	117.7
C2-C3-C4	126.8(2)
C2-C3-Co	64.36(13)
C4-C3-Co	108.69(15)
C2-C3-H3A	114.9
C4-C3-H3A	114.9
Co-C3-H3A	114.9
C3-C4-C5	109.3(2)
C3-C4-H4A	109.8
C5-C4-H4A	109.8
C3-C4-H4B	109.8
C5-C4-H4B	109.8
H4A-C4-H4B	108.3
C6-C5-C4	110.5(2)
C6-C5-H5A	109.6
C4-C5-H5A	109.6
C6-C5-H5B	109.6
C4-C5-H5B	109.6
H5A-C5-H5B	108.1
C7-C6-C5	116.1(2)
C7-C6-Co	108.49(17)
C5-C6-Co	106.45(17)
C7-C6-H6A	108.5
C5-C6-H6A	108.5
Co-C6-H6A	108.5
C6-C7-C8	111.4(2)
C6-C7-H7A	109.4
C8-C7-H7A	109.4

C6-C7-H7B	109.4
C8-C7-H7B	109.4
H7A-C7-H7B	108.0
C1-C8-C7	110.8(2)
C1-C8-H8A	109.5
C7-C8-H8A	109.5
C1-C8-H8B	109.5
C7-C8-H8B	109.5
H8A-C8-H8B	108.1
C10-O1-Co	125.46(15)
C12-N1-C14	117.17(19)
C12-N1-Co	124.31(16)
C14-N1-Co	118.52(14)
C10-C9-H9A	109.5
C10-C9-H9B	109.5
H9A-C9-H9B	109.5
C10-C9-H9C	109.5
H9A-C9-H9C	109.5
H9B-C9-H9C	109.5
O1-C10-C11	124.7(2)
O1-C10-C9	115.1(2)
C11-C10-C9	120.1(2)
C10-C11-C12	126.4(2)
C10-C11-H11A	116.8
C12-C11-H11A	116.8
N1-C12-C11	122.5(2)
N1-C12-C13	121.5(2)
C11-C12-C13	115.9(2)
C12-C13-H13A	109.5
C12-C13-H13B	109.5
H13A-C13-H13B	109.5
C12-C13-H13C	109.5
H13A-C13-H13C	109.5
H13B-C13-H13C	109.5
C19-C14-C15	119.2(2)
C19-C14-N1	119.9(2)
C15-C14-N1	120.8(2)
C16-C15-C14	120.6(2)
C16-C15-H15A	119.7
C14-C15-H15A	119.7
C17-C16-C15	120.2(2)
C17-C16-H16A	119.9
C15-C16-H16A	119.9
C16-C17-C18	119.6(2)
C16-C17-H17A	120.2
C18-C17-H17A	120.2
C17-C18-C19	120.7(2)
C17-C18-H18A	119.7
C19-C18-H18A	119.7
C14-C19-C18	119.7(2)
C14-C19-H19A	120.1
C18-C19-H19A	120.1

Table A1.4. Anisotropic displacement parameters ($Å^2$x 10^3)for **21**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Co	18(1)	27(1)	24(1)	2(1)	-8(1)	-11(1)
C1	22(1)	30(1)	56(2)	4(1)	-14(1)	-14(1)
C2	21(1)	39(2)	43(1)	-8(1)	-14(1)	-12(1)
C3	24(1)	43(2)	29(1)	3(1)	-13(1)	-14(1)
C4	30(1)	33(1)	38(1)	6(1)	-13(1)	-8(1)
C5	42(2)	27(1)	40(1)	2(1)	-15(1)	-11(1)
C6	34(1)	26(1)	31(1)	0(1)	-15(1)	-10(1)
C7	40(2)	38(2)	26(1)	0(1)	-3(1)	-5(1)
C8	27(1)	48(2)	47(2)	15(1)	-2(1)	-15(1)
O1	24(1)	37(1)	28(1)	9(1)	-10(1)	-16(1)
N1	21(1)	24(1)	27(1)	2(1)	-8(1)	-12(1)
C9	32(1)	36(1)	38(1)	1 (1)	-11(1)	-20(1)
C10	24(1)	28(1)	27(1)	0(1)	-7(1)	-14(1)
C11	22(1)	29(1)	34(1)	2(1)	-10(1)	-14(1)
C12	19(1)	26(1)	26(1)	-1(1)	-8(1)	-8(1)
C13	24(1)	34(1)	40(1)	1 (1)	-15(1)	-11(1)
C14	21(1)	27(1)	28(1)	4(1)	-11(1)	-12(1)
C15	31(1)	35(1)	28(1)	2(1)	-11(1)	-16(1)
C16	37(1)	45(2)	27(1)	11(1)	-1 (1)	-20(1)
C17	42(2)	38(2)	45(2)	18(1)	-17(1)	-23(1)
C18	42(2)	28(1)	41(1)	2(1)	-14(1)	-19(1)
C19	30(1)	29(1)	26(1)	1(1)	-8(1)	-14(1)

Table A1.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **21**.

Atom	x	y	z	U(eq)
H1A	1855	-440	2317	41
H2A	1866	516	512	40
H3A	1790	2965	96	37
H4A	-756	4240	2250	41
H4B	-74	5220	1277	41
H5A	2105	5059	2040	44
H5B	491	5430	3163	44
H6A	3146	3280	3268	36
H7A	302	3438	4512	48
H7B	1916	1836	4399	48
H8A	9	963	4043	51
H8B	-774	2428	3363	51
H9A	6529	3902	-318	50
H9B	8352	2545	-421	50
H9C	7497	3907	611	50
H11A	8206	1342	1698	32
H13A	7600	-1862	3076	47
H13B	8300	-587	3264	47
H13C	9106	-1676	2072	47
H15A	4332	-417	4505	36
H16A	3726	-2460	5427	42
H17A	3896	-4565	4318	47
H18A	4750	-4664	2275	42
H19A	5384	-2635	1336	33

Table A1.6. Torsion angles [°] for **21**.

O1-Co-C1-C2	20.4(5)
N1-Co-C1-C2	-145.32(15)
C6-Co-C1-C2	116.30(17)
C3-Co-C1-C2	29.70(16)
O1-Co-C1-C8	-100.3(4)
N1-Co-C1-C8	93.96(19)
C2-Co-C1-C8	-120.7(3)
C6-Co-C1-C8	-4.42(19)
C3-Co-C1-C8	-91.0(2)
C8-C1-C2-C3	38.1(4)
Co-C1-C2-C3	-59.2(2)
C8-C1-C2-Co	97.3(2)
O1-Co-C2-C3	-41.07(19)
N1-Co-C2-C3	-179.05(13)
C6-Co-C2-C3	65.69(17)
C1-Co-C2-C3	132.8(2)
O1-Co-C2-C1	-173.85(14)
N1-Co-C2-C1	48.2(2)
C6-Co-C2-C1	-67.09(17)
C3-Co-C2-C1	-132.8(2)
C1-C2-C3-C4	-36.3(4)
Co-C2-C3-C4	-94.9(2)
C1-C2-C3-Co	58.5(2)
O1-Co-C3-C2	147.52(15)
N1-Co-C3-C2	4.8(7)
C6-Co-C3-C2	-117.43(16)
C1-Co-C3-C2	-30.14(16)
O1-Co-C3-C4	-89.88(17)
N1-Co-C3-C4	127.4(5)
C2-Co-C3-C4	122.6(2)
C6-Co-C3-C4	5.17(18)
C1-Co-C3-C4	92.45(19)
C2-C3-C4-C5	90.7(3)
Co-C3-C4-C5	19.2(3)
C3-C4-C5-C6	-43.9(3)
C4-C5-C6-C7	-73.6(3)
C4-C5-C6-Co	47.3(3)
O1-Co-C6-C7	-170.45(17)
N1-Co-C6-C7	-75.16(18)
C2-Co-C6-C7	61.3(2)
C1-Co-C6-C7	24.08(18)
C3-Co-C6-C7	97.50(19)
O1-Co-C6-C5	63.87(18)
N1-Co-C6-C5	159.16(18)
C2-Co-C6-C5	-64.4(2)
C1-Co-C6-C5	-101.60(19)
C3-Co-C6-C5	-28.18(19)
C5-C6-C7-C8	80.1(3)
Co-C6-C7-C8	-39.7(3)
C2-C1-C8-C7	-89.1(3)
Co-C1-C8-C7	-16.2(3)

C6-C7-C8-C1	36.7(3)
N1-Co-O1-C10	-13.5(2)
C2-Co-O1-C10	-163.17(19)
C6-Co-O1-C10	85.8(2)
C1-Co-O1-C10	-179.4(3)
C3-Co-O1-C10	171.7(2)
O1-Co-N1-C12	12.34(19)
C2-Co-N1-C12	159.10(18)
C6-Co-N1-C12	-83.6(2)
C1-Co-N1-C12	-171.23(19)
C3-Co-N1-C12	155.0(5)
O1-Co-N1-C14	-168.43(16)
C2-Co-N1-C14	-21.7(2)
C6-Co-N1-C14	95.58(17)
C1-Co-N1-C14	8.00(18)
C3-Co-N1-C14	-25.8(7)
Co-O1-C10-C11	5.7(3)
Co-O1-C10-C9	-177.85(16)
O1-C10-C11-C12	8.7(4)
C9-C10-C11-C12	-167.6(2)
C14-N1-C12-C11	177.1(2)
Co-N1-C12-C11	-3.7(3)
C14-N1-C12-C13	0.3(3)
Co-N1-C12-C13	179.57(16)
C10-C11-C12-N1	-9.6(4)
C10-C11-C12-C13	167.4(2)
C12-N1-C14-C19	-105.5(3)
Co-N1-C14-C19	75.2(2)
C12-N1-C14-C15	77.2(3)
Co-N1-C14-C15	-102.1(2)
C19-C14-C15-C16	0.0(4)
N1-C14-C15-C16	177.3(2)
C14-C15-C16-C17	-0.6(4)
C15-C16-C17-C18	0.9(4)
C16-C17-C18-C19	-0.6(4)
C15-C14-C19-C18	0.2(4)
N1-C14-C19-C18	-177.1(2)
C17-C18-C19-C14	0.0(4)

Crystallographic Data for $CH_3C(NPh)CHC(NPh)CH_3CoC_8H_{12}$, **12.**

Table A2.1. Crystal data and structure refinement for **12**.

Empirical formula	C25 H29 Co N2	
Formula weight	416.43	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Cmc2(1)	
Unit cell dimensions	a = 20.8330(2) Å	α= 90°.
	b = 13.0171(3) Å	β= 90°.
	c = 7.6855(1) Å	γ = 90°.
Volume	2084.19(6) $Å^3$	
Z	4	
Density (calculated)	1.327 Mg/m^3	
Absorption coefficient	0.836 mm^{-1}	
F(000)	880	
Crystal size	0.26 x 0.07 x 0.05 mm^3	
Theta range for data collection	1.84 to 27.48°.	
Index ranges	$-26 \leq h \leq 27$, $-16 \leq k \leq 15$, $-9 \leq l \leq 8$	
Reflections collected	6859	
Independent reflections	2241 [R(int) = 0.0426]	
Completeness to theta = 27.48°	100.0 %	
Absorption correction	Empirical	
Max. and min. transmission	0.962 and 0.800	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2241 / 1 / 134	
Goodness-of-fit on F^2	1.054	
Final R indices [I>2sigma(I)]	R1 = 0.0366, wR2 = 0.0816 [2024]	
R indices (all data)	R1 = 0.0449, wR2 = 0.0861	
Absolute structure parameter	0.04(2)	
Extinction coefficient	0.0005(3)	
Largest diff. peak and hole	0.402 and -0.351 e.$Å^{-3}$	

Table A2.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **12**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
Co	0	2019(1)	7907(1)	21(1)
C1	0	654(3)	9001(6)	34(1)
C2	-602(1)	1080(2)	9448(4)	32(1)
C3	-761(2)	1645(3)	11100(5)	45(1)
C4	-613(2)	2799(3)	10927(5)	45(1)
C5	0	2957(3)	9917(6)	33(1)
C6	-1166(1)	4206(2)	5114(5)	35(1)
C7	-601(1)	3625(2)	5898(4)	26(1)
C8	0	4089(3)	5678(6)	29(1)
N1	-676(1)	2716(2)	6650(3)	23(1)
C9	-1301(1)	2247(2)	6626(4)	26(1)
C10	-1816(1)	2629(2)	7582(5)	32(1)
C11	-2401(1)	2108(2)	7579(5)	39(1)
C12	-2474(2)	1219(3)	6648(5)	40(1)
C13	-1968(1)	833(2)	5681(4)	35(1)
C14	-1380(1)	1347(2)	5665(4)	29(1)

Table A2.3. Bond lengths [Å] and angles [°] for **12**.

Co-N1	1.935(2)
Co-N1#1	1.935(2)
Co-C1	1.965(4)
Co-C5	1.969(4)
Co-C2#1	2.113(3)
Co-C2	2.113(3)
C1-C2	1.413(4)
C1-C2#1	1.413(4)
C2-C3	1.504(5)
C3-C4	1.538(5)
C4-C5	1.509(4)
C5-C4#1	1.509(4)
C6-C7	1.524(4)
C7-N1	1.326(4)
C7-C8	1.400(3)
C8-C7#1	1.400(3)
N1-C9	1.436(3)
C9-C10	1.393(4)
C9-C14	1.394(4)
C10-C11	1.395(4)
C11-C12	1.369(5)
C12-C13	1.383(5)
C13-C14	1.396(4)

N1-Co-N1#1	93.53(14)
N1-Co-C1	129.60(8)
N1#1-Co-C1	129.60(8)
N1-Co-C5	95.79(11)
N1#1-Co-C5	95.79(12)
C1-Co-C5	103.01(19)
N1-Co-C2#1	169.43(11)
N1#1-Co-C2#1	96.81(11)
C1-Co-C2#1	40.34(10)
C5-Co-C2#1	85.36(15)
N1-Co-C2	96.82(11)
N1#1-Co-C2	169.43(11)
C1-Co-C2	40.34(10)
C5-Co-C2	85.36(15)
C2#1-Co-C2	72.77(16)
C2-C1-C2#1	125.0(4)
C2-C1-Co	75.5(2)
C2#1-C1-Co	75.5(2)
C1-C2-C3	126.4(3)
C1-C2-Co	64.17(19)
C3-C2-Co	108.7(2)
C2-C3-C4	111.1(3)
C5-C4-C3	110.3(3)
C4-C5-C4#1	115.6(4)
C4-C5-Co	108.6(2)
C4#1-C5-Co	108.6(2)
N1-C7-C8	122.9(3)

N1-C7-C6	121.6(2)
C8-C7-C6	115.4(3)
C7#1-C8-C7	126.8(3)
C7-N1-C9	118.7(2)
C7-N1-Co	123.34(18)
C9-N1-Co	117.83(18)
C10-C9-C14	119.2(3)
C10-C9-N1	122.6(3)
C14-C9-N1	118.1(2)
C9-C10-C11	119.9(3)
C12-C11-C10	120.6(3)
C11-C12-C13	120.2(3)
C12-C13-C14	119.9(3)
C9-C14-C13	120.2(3)

Symmetry transformations used to generate equivalent atoms: #1 -x,y,z

Table A2.4. Anisotropic displacement parameters ($Å^2$x 10^3)for **12**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Co	20(1)	18(1)	26(1)	1(1)	0	0
C1	35(2)	20(2)	47(3)	13(2)	0	0
C2	28(1)	28(2)	38(2)	13(1)	0(1)	-3(1)
C3	39(2)	61(2)	37(2)	19(2)	11(2)	8(2)
C4	52(2)	53(2)	30(2)	-6(2)	3(2)	12(2)
C5	45(3)	24(2)	28(2)	-8(2)	0	0
C6	28(2)	31(2)	46(2)	5(1)	-4(1)	8(1)
C7	25(1)	22(1)	30(2)	-1(1)	-2(1)	5(1)
C8	27(2)	20(2)	40(2)	7(2)	0	0
N1	19(1)	22(1)	27(1)	0(1)	0(1)	0(1)
C9	20(1)	28(2)	29(2)	1(1)	1(1)	1(1)
C10	24(1)	33(1)	40(2)	-6(1)	3(1)	0(1)
C11	22(1)	48(2)	47(3)	-2(2)	10(1)	-2(1)
C12	25(1)	46(2)	47(2)	1(2)	0(1)	-10(1)
C13	36(2)	31(2)	39(2)	-5(1)	-5(2)	-9(1)
C14	25(1)	33(2)	30(2)	-2(1)	1(1)	-1(1)

Table A2.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **12**.

Atom	x	y	z	U(eq)
H1A	0	43	8212	41
H2A	-978	777	8824	38
H3A	-509	1354	12073	54
H3B	-1222	1552	11371	54
H4A	-972	3147	10323	54
H4B	-569	3106	12099	54
H5A	0	3677	9463	39
H6A	-1563	3825	5333	53
H6B	-1102	4280	3857	53
H6C	-1196	4888	5649	53
H8A	0	4791	5344	34
H10A	-1769	3244	8236	39
H11A	-2752	2372	8228	47
H12A	-2873	866	6666	47
H13A	-2021	219	5029	42
H14A	-1034	1084	4998	35

Table A2.6. Torsion angles [°] for **12**.

N1-Co-C1-C2	-42.6(3)
N1#1-Co-C1-C2	175.40(19)
C5-Co-C1-C2	66.4(2)
C2#1-Co-C1-C2	132.8(4)
N1-Co-C1-C2#1	-175.40(19)
N1#1-Co-C1-C2#1	42.6(3)
C5-Co-C1-C2#1	-66.4(2)
C2-Co-C1-C2#1	-132.8(4)
C2#1-C1-C2-C3	-34.8(6)
Co-C1-C2-C3	-95.0(3)
C2#1-C1-C2-Co	60.2(4)
N1-Co-C2-C1	148.3(2)
N1#1-Co-C2-C1	-19.7(8)
C5-Co-C2-C1	-116.4(2)
C2#1-Co-C2-C1	-29.8(3)
N1-Co-C2-C3	-89.6(2)
N1#1-Co-C2-C3	102.4(7)
C1-Co-C2-C3	122.1(3)
C5-Co-C2-C3	5.7(2)
C2#1-Co-C2-C3	92.3(2)
C1-C2-C3-C4	87.7(4)
Co-C2-C3-C4	16.5(3)
C2-C3-C4-C5	-39.0(4)
C3-C4-C5-C4#1	-79.2(4)
C3-C4-C5-Co	43.1(4)
N1-Co-C5-C4	69.7(3)
N1#1-Co-C5-C4	163.8(3)
C1-Co-C5-C4	-63.3(3)
C2#1-Co-C5-C4	-99.8(3)
C2-Co-C5-C4	-26.7(3)
N1-Co-C5-C4#1	-163.8(3)
N1#1-Co-C5-C4#1	-69.7(3)
C1-Co-C5-C4#1	63.3(3)
C2#1-Co-C5-C4#1	26.7(3)
C2-Co-C5-C4#1	99.8(3)
N1-C7-C8-C7#1	12.3(7)
C6-C7-C8-C7#1	-164.2(3)
C8-C7-N1-C9	-172.5(3)
C6-C7-N1-C9	3.8(4)
C8-C7-N1-Co	11.4(4)
C6-C7-N1-Co	-172.4(2)
N1#1-Co-N1-C7	-24.9(3)
C1-Co-N1-C7	-176.5(3)
C5-Co-N1-C7	71.3(2)
C2#1-Co-N1-C7	167.0(6)
C2-Co-N1-C7	157.3(2)
N1#1-Co-N1-C9	158.89(16)
C1-Co-N1-C9	7.3(3)
C5-Co-N1-C9	-104.9(2)
C2#1-Co-N1-C9	-9.2(8)
C2-Co-N1-C9	-18.9(2)

C7-N1-C9-C10	-69.7(4)
Co-N1-C9-C10	106.7(3)
C7-N1-C9-C14	113.3(3)
Co-N1-C9-C14	-70.3(3)
C14-C9-C10-C11	0.4(5)
N1-C9-C10-C11	-176.5(3)
C9-C10-C11-C12	0.3(5)
C10-C11-C12-C13	-0.7(5)
C11-C12-C13-C14	0.5(5)
C10-C9-C14-C13	-0.7(4)
N1-C9-C14-C13	176.4(3)
C12-C13-C14-C9	0.2(5)

Symmetry transformations used to generate equivalent atoms: #1 -x,y,z

Crystallographic Data for TpCoC$_8$H$_{12}$, **23**.

Table A3.1. Crystal data and structure refinement for **23**.

Empirical formula	C17 H22 B Co N6	
Formula weight	380.15	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.4684(5) Å	α= 90°.
	b = 12.6147(6) Å	β= 90°.
	c = 13.0965(7) Å	γ = 90°.
Volume	1729.47(15) Å^3	
Z	4	
Density (calculated)	1.460 Mg/m^3	
Absorption coefficient	1.005 mm^{-1}	
F(000)	792	
Crystal size	0.10 x 0.17 x 0.17 mm^3	
Theta range for data collection	2.24 to 27.50°.	
Index ranges	$-13 \leq h \leq 11$, $-16 \leq k \leq 16$, $-15 \leq l \leq 17$	
Reflections collected	11371	
Independent reflections	4293 [R(int) = 0.0229]	
Completeness to theta = 27.50°	99.8 %	
Absorption correction	Integration	
Max. and min. transmission	0.924 and 0.837	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3951 / 0 / 231	
Goodness-of-fit on F^2	0.985	
Final R indices [I>2sigma(I)]	R1 = 0.0233, wR2 = 0.0504 [3611]	
R indices (all data)	R1 = 0.0282, wR2 = 0.0519	
Absolute structure parameter	-0.001(10)	
Extinction coefficient	0.0012(3)	
Largest diff. peak and hole	0.204 and -0.182 e.Å^{-3}	

Table A3.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **23**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
Co	5344(1)	-446(1)	8236(1)	20(1)
B	7807(2)	619(2)	7363(2)	26(1)
N1	5577(1)	166(1)	6850(1)	23(1)
C1	4723(2)	-1246(1)	9549(1)	33(1)
N2	6683(1)	683(1)	6621(1)	24(1)
C2	4672(2)	-1855(1)	8649(2)	33(1)
N3	6430(1)	644(1)	8923(1)	22(1)
C3	3998(2)	-1583(1)	7769(2)	33(1)
N4	7433(1)	1078(1)	8410(1)	24(1)
C4	2661(2)	-1112(2)	7738(2)	40(1)
N5	7148(1)	-1211(1)	7940(1)	23(1)
C5	2703(2)	102(2)	7791(2)	35(1)
N6	8086(1)	-576(1)	7552(1)	23(1)
C6	3788(2)	465(2)	8480(1)	27(1)
C7	3427(2)	437(2)	9609(1)	36(1)
C8	3602(2)	-684(2)	10039(2)	40(1)
C9	4898(2)	151(1)	5982(1)	31(1)
C10	5542(2)	666(2)	5204(1)	36(1)
C11	6667(2)	985(2)	5630(1)	31(1)
C12	6499(2)	1037(2)	9870(1)	30(1)
C13	7525(2)	1726(2)	9973(2)	37(1)
C14	8101(2)	1725(1)	9038(2)	32(1)
C15	7686(2)	-2158(1)	8062(1)	29(1)
C16	8969(2)	-2144(2)	7766(2)	34(1)
C17	9181(2)	-1116(2)	7455(1)	30(1)

Table A3.3. Bond lengths [Å] and angles [°] for **23**.

Co-C2	1.9864(17)
Co-N1	1.9881(15)
Co-N3	1.9984(14)
Co-C6	2.0190(17)
Co-C1	2.0962(18)
Co-C3	2.1015(18)
Co-N5	2.1548(15)
B-N2	1.529(2)
B-N4	1.539(2)
B-N6	1.555(3)
B-H1	1.094(19)
N1-C9	1.341(2)
N1-N2	1.3619(19)
C1-C2	1.407(3)
C1-C8	1.515(3)
C1-H1A	1.0000
N2-C11	1.353(2)
C2-C3	1.395(3)
C2-H2A	1.0000
N3-C12	1.337(2)
N3-N4	1.3611(19)
C3-C4	1.521(3)
C3-H3A	1.0000
N4-C14	1.352(2)
C4-C5	1.533(3)
C4-H4A	0.9900
C4-H4B	0.9900
N5-C15	1.330(2)
N5-N6	1.366(2)
C5-C6	1.522(3)
C5-H5A	0.9900
C5-H5B	0.9900
N6-C17	1.339(2)
C6-C7	1.526(2)
C6-H6A	1.0000
C7-C8	1.534(3)
C7-H7A	0.9900
C7-H7B	0.9900
C8-H8A	0.9900
C8-H8B	0.9900
C9-C10	1.384(3)
C9-H9A	0.9500
C10-C11	1.364(3)
C10-H10A	0.9500
C11-H11A	0.9500
C12-C13	1.389(3)
C12-H12A	0.9500
C13-C14	1.366(3)
C13-H13A	0.9500
C14-H14A	0.9500
C15-C16	1.398(3)

C15-H15A	0.9500
C16-C17	1.377(3)
C16-H16A	0.9500
C17-H17A	0.9500

C2-Co-N1	129.77(7)
C2-Co-N3	134.03(7)
N1-Co-N3	94.21(5)
C2-Co-C6	100.40(8)
N1-Co-C6	91.25(6)
N3-Co-C6	89.78(7)
C2-Co-C1	40.21(8)
N1-Co-C1	166.85(7)
N3-Co-C1	97.99(7)
C6-Co-C1	83.94(8)
C2-Co-C3	39.77(8)
N1-Co-C3	94.67(7)
N3-Co-C3	169.19(7)
C6-Co-C3	83.87(8)
C1-Co-C3	72.69(8)
C2-Co-N5	87.65(7)
N1-Co-N5	84.38(5)
N3-Co-N5	83.72(5)
C6-Co-N5	171.87(7)
C1-Co-N5	101.76(7)
C3-Co-N5	103.28(7)
N2-B-N4	110.52(15)
N2-B-N6	107.25(14)
N4-B-N6	105.74(14)
N2-B-H1	110.8(10)
N4-B-H1	112.5(10)
N6-B-H1	109.8(10)
C9-N1-N2	105.70(14)
C9-N1-Co	134.71(12)
N2-N1-Co	119.45(10)
C2-C1-C8	125.55(19)
C2-C1-Co	65.69(10)
C8-C1-Co	111.26(12)
C2-C1-H1A	114.7
C8-C1-H1A	114.7
Co-C1-H1A	114.7
C11-N2-N1	109.63(15)
C11-N2-B	129.36(16)
N1-N2-B	119.26(13)
C3-C2-C1	125.22(17)
C3-C2-Co	74.56(10)
C1-C2-Co	74.10(10)
C3-C2-H2A	117.0
C1-C2-H2A	117.0
Co-C2-H2A	117.0
C12-N3-N4	105.47(14)
C12-N3-Co	134.65(13)
N4-N3-Co	119.60(10)
C2-C3-C4	125.74(19)

C2-C3-Co	65.66(10)
C4-C3-Co	111.01(13)
C2-C3-H3A	114.7
C4-C3-H3A	114.7
Co-C3-H3A	114.7
C14-N4-N3	109.99(15)
C14-N4-B	129.54(16)
N3-N4-B	118.96(14)
C3-C4-C5	111.24(18)
C3-C4-H4A	109.4
C5-C4-H4A	109.4
C3-C4-H4B	109.4
C5-C4-H4B	109.4
H4A-C4-H4B	108.0
C15-N5-N6	105.43(15)
C15-N5-Co	138.71(13)
N6-N5-Co	115.78(10)
C6-C5-C4	110.43(17)
C6-C5-H5A	109.6
C4-C5-H5A	109.6
C6-C5-H5B	109.6
C4-C5-H5B	109.6
H5A-C5-H5B	108.1
C17-N6-N5	110.65(15)
C17-N6-B	129.68(16)
N5-N6-B	119.50(13)
C5-C6-C7	112.52(16)
C5-C6-Co	109.71(12)
C7-C6-Co	109.87(12)
C5-C6-H6A	108.2
C7-C6-H6A	108.2
Co-C6-H6A	108.2
C6-C7-C8	110.34(17)
C6-C7-H7A	109.6
C8-C7-H7A	109.6
C6-C7-H7B	109.6
C8-C7-H7B	109.6
H7A-C7-H7B	108.1
C1-C8-C7	111.62(15)
C1-C8-H8A	109.3
C7-C8-H8A	109.3
C1-C8-H8B	109.3
C7-C8-H8B	109.3
H8A-C8-H8B	108.0
N1-C9-C10	111.06(17)
N1-C9-H9A	124.5
C10-C9-H9A	124.5
C11-C10-C9	104.94(16)
C11-C10-H10A	127.5
C9-C10-H10A	127.5
N2-C11-C10	108.65(17)
N2-C11-H11A	125.7
C10-C11-H11A	125.7
N3-C12-C13	111.36(17)

N3-C12-H12A	124.3
C13-C12-H12A	124.3
C14-C13-C12	104.64(17)
C14-C13-H13A	127.7
C12-C13-H13A	127.7
N4-C14-C13	108.52(18)
N4-C14-H14A	125.7
C13-C14-H14A	125.7
N5-C15-C16	111.25(17)
N5-C15-H15A	124.4
C16-C15-H15A	124.4
C17-C16-C15	104.42(17)
C17-C16-H16A	127.8
C15-C16-H16A	127.8
N6-C17-C16	108.23(18)
N6-C17-H17A	125.9
C16-C17-H17A	125.9

Table A3.4. Anisotropic displacement parameters (Å^{2}x 10^3)for **23**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Co	18(1)	19(1)	22(1)	2(1)	1(1)	0(1)
B	23(1)	30(1)	26(1)	4(1)	3(1)	-4(1)
N1	23(1)	24(1)	22(1)	-1(1)	0(1)	1(1)
C1	28(1)	34(1)	38(1)	16(1)	3(1)	0(1)
N2	25(1)	24(1)	22(1)	2(1)	4(1)	2(1)
C2	26(1)	19(1)	54(1)	9(1)	6(1)	-4(1)
N3	23(1)	22(1)	21(1)	1(1)	0(1)	0(1)
C3	25(1)	24(1)	50(1)	-4(1)	1(1)	-5(1)
N4	24(1)	23(1)	25(1)	1(1)	0(1)	-4(1)
C4	26(1)	37(1)	57(1)	-4(1)	-4(1)	-4(1)
N5	23(1)	24(1)	23(1)	0(1)	-1(1)	0(1)
C5	22(1)	36(1)	49(1)	-1(1)	-3(1)	5(1)
N6	19(1)	30(1)	22(1)	0(1)	1(1)	1(1)
C6	22(1)	22(1)	36(1)	1(1)	2(1)	2(1)
C7	28(1)	42(1)	37(1)	-2(1)	10(1)	7(1)
C8	37(1)	49(1)	36(1)	9(1)	14(1)	-1(1)
C9	31(1)	33(1)	28(1)	-5(1)	-7(1)	4(1)
C10	47(1)	40(1)	19(1)	0(1)	-4(1)	13(1)
C11	42(1)	30(1)	22(1)	4(1)	1 (1)	1 (1)
C12	36(1)	30(1)	23(1)	-2(1)	-1(1)	2(1)
C13	49(1)	31(1)	31(1)	-5(1)	-12(1)	-4(1)
C14	37(1)	23(1)	36(1)	1(1)	-7(1)	-6(1)
C15	32(1)	26(1)	30(1)	-2(1)	-3(1)	8(1)
C16	31(1)	39(1)	33(1)	-2(1)	1(1)	15(1)
C17	22(1)	45(1)	21(1)	-3(1)	-1(1)	6(1)

Table A3.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **23**.

Atom	x	y	z	U(eq)
H1	8653(18)	1004(15)	7042(14)	31(5)
H1A	5420	-1451	10032	40
H2A	5271	-2471	8599	40
H3A	4245	-1992	7146	40
H4A	2157	-1388	8319	48
H4B	2231	-1332	7099	48
H5A	2827	394	7096	42
H5B	1881	372	8059	42
H6A	4008	1212	8295	32
H7A	2526	660	9691	43
H7B	3972	940	9993	43
H8A	3741	-641	10786	49
H8B	2814	-1099	9920	49
H9A	4083	-171	5911	37
H10A	5262	774	4522	43
H11A	7330	1357	5288	37
H12A	5919	867	10403	35
H13A	7772	2112	10564	44
H14A	8846	2113	8857	38
H15A	7255	-2765	8317	35
H16A	9560	-2714	7776	41
H17A	9968	-838	7214	35

Table A3.6. Torsion angles [°] for **23**.

C2-Co-N1-C9	39.73(19)
N3-Co-N1-C9	-154.80(16)
C6-Co-N1-C9	-64.94(16)
C1-Co-N1-C9	3.3(4)
C3-Co-N1-C9	19.02(17)
N5-Co-N1-C9	121.94(16)
C2-Co-N1-N2	-135.21(12)
N3-Co-N1-N2	30.26(11)
C6-Co-N1-N2	120.13(11)
C1-Co-N1-N2	-171.6(3)
C3-Co-N1-N2	-155.92(11)
N5-Co-N1-N2	-53.00(11)
N1-Co-C1-C2	45.0(3)
N3-Co-C1-C2	-157.07(12)
C6-Co-C1-C2	114.01(13)
C3-Co-C1-C2	28.56(12)
N5-Co-C1-C2	-71.87(13)
C2-Co-C1-C8	-120.6(2)
N1-Co-C1-C8	-75.6(3)
N3-Co-C1-C8	82.34(15)
C6-Co-C1-C8	-6.58(14)
C3-Co-C1-C8	-92.03(15)
N5-Co-C1-C8	167.55(14)
C9-N1-N2-C11	0.53(17)
Co-N1-N2-C11	176.80(11)
C9-N1-N2-B	-165.81(15)
Co-N1-N2-B	10.46(18)
N4-B-N2-C11	136.32(17)
N6-B-N2-C11	-108.87(18)
N4-B-N2-N1	-60.40(19)
N6-B-N2-N1	54.41(19)
C8-C1-C2-C3	42.2(3)
Co-C1-C2-C3	-57.33(18)
C8-C1-C2-Co	99.57(17)
N1-Co-C2-C3	-33.43(15)
N3-Co-C2-C3	166.93(11)
C6-Co-C2-C3	67.03(12)
C1-Co-C2-C3	134.49(18)
N5-Co-C2-C3	-114.13(12)
N1-Co-C2-C1	-167.92(11)
N3-Co-C2-C1	32.45(16)
C6-Co-C2-C1	-67.45(13)
C3-Co-C2-C1	-134.49(18)
N5-Co-C2-C1	111.39(12)
C2-Co-N3-C12	-40.3(2)
N1-Co-N3-C12	155.25(17)
C6-Co-N3-C12	64.01(17)
C1-Co-N3-C12	-19.83(18)
C3-Co-N3-C12	10.1(5)
N5-Co-N3-C12	-120.88(17)
C2-Co-N3-N4	132.71(13)

N1-Co-N3-N4	-31.73(12)
C6-Co-N3-N4	-122.97(12)
C1-Co-N3-N4	153.19(12)
C3-Co-N3-N4	-176.9(3)
N5-Co-N3-N4	52.14(12)
C1-C2-C3-C4	-42.0(3)
Co-C2-C3-C4	-99.17(18)
C1-C2-C3-Co	57.12(17)
N1-Co-C3-C2	154.86(11)
N3-Co-C3-C2	-60.0(4)
C6-Co-C3-C2	-114.38(12)
C1-Co-C3-C2	-28.85(12)
N5-Co-C3-C2	69.54(12)
C2-Co-C3-C4	120.9(2)
N1-Co-C3-C4	-84.28(15)
N3-Co-C3-C4	60.8(4)
C6-Co-C3-C4	6.49(15)
C1-Co-C3-C4	92.02(16)
N5-Co-C3-C4	-169.59(14)
C12-N3-N4-C14	0.06(19)
Co-N3-N4-C14	-174.79(12)
C12-N3-N4-B	167.35(15)
Co-N3-N4-B	-7.50(19)
N2-B-N4-C14	-137.11(18)
N6-B-N4-C14	107.14(19)
N2-B-N4-N3	58.44(19)
N6-B-N4-N3	-57.31(18)
C2-C3-C4-C5	88.7(3)
Co-C3-C4-C5	14.2(2)
C2-Co-N5-C15	-6.63(19)
N1-Co-N5-C15	-136.97(19)
N3-Co-N5-C15	128.15(19)
C6-Co-N5-C15	165.3(4)
C1-Co-N5-C15	31.3(2)
C3-Co-N5-C15	-43.5(2)
C2-Co-N5-N6	177.12(12)
N1-Co-N5-N6	46.77(11)
N3-Co-N5-N6	-48.11(11)
C6-Co-N5-N6	-11.0(5)
C1-Co-N5-N6	-145.00(11)
C3-Co-N5-N6	140.25(12)
C3-C4-C5-C6	-35.4(3)
C15-N5-N6-C17	-1.11(18)
Co-N5-N6-C17	176.33(11)
C15-N5-N6-B	-176.90(15)
Co-N5-N6-B	0.54(18)
N2-B-N6-C17	126.44(18)
N4-B-N6-C17	-115.60(18)
N2-B-N6-N5	-58.69(18)
N4-B-N6-N5	59.28(18)
C4-C5-C6-C7	-82.1(2)
C4-C5-C6-Co	40.6(2)
C2-Co-C6-C5	-62.10(14)
N1-Co-C6-C5	68.79(13)

N3-Co-C6-C5	163.00(13)
C1-Co-C6-C5	-98.94(14)
C3-Co-C6-C5	-25.77(14)
N5-Co-C6-C5	126.1(4)
C2-Co-C6-C7	62.09(15)
N1-Co-C6-C7	-167.02(13)
N3-Co-C6-C7	-72.81(13)
C1-Co-C6-C7	25.25(14)
C3-Co-C6-C7	98.42(14)
N5-Co-C6-C7	-109.7(4)
C5-C6-C7-C8	83.1(2)
Co-C6-C7-C8	-39.41(19)
C2-C1-C8-C7	-88.2(2)
Co-C1-C8-C7	-13.6(2)
C6-C7-C8-C1	34.3(2)
N2-N1-C9-C10	-1.02(18)
Co-N1-C9-C10	-176.44(12)
N1-C9-C10-C11	1.1(2)
N1-N2-C11-C10	0.15(19)
B-N2-C11-C10	164.69(17)
C9-C10-C11-N2	-0.7(2)
N4-N3-C12-C13	0.5(2)
Co-N3-C12-C13	174.20(13)
N3-C12-C13-C14	-0.8(2)
N3-N4-C14-C13	-0.6(2)
B-N4-C14-C13	-166.14(17)
C12-C13-C14-N4	0.8(2)
N6-N5-C15-C16	0.6(2)
Co-N5-C15-C16	-175.95(14)
N5-C15-C16-C17	0.2(2)
N5-N6-C17-C16	1.25(19)
B-N6-C17-C16	176.48(17)
C15-C16-C17-N6	-0.9(2)

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BIOGRAPHICAL SKETCH

Jonathan Michael Penney was born September 13, 1971 and grew up in Andover, Massachusetts. His interest in science began in elementary school and his decision to pursue chemistry occurred during high school. He completed his undergraduate study with a bachelors degree in science from the University of Massachusetts, Amherst, in 1993. While pursuing his undergraduate degree he was exposed to organometallic chemistry by participating in research for Dr. Marvin Rausch. Before meeting Dr. Rausch, graduate studies were never considered. After spending a year working for Dr. Rausch, a graduate career became the only option. In the fall of 1993 Jon started graduate school at the University of Florida. Immediately, he joined the research group of Dr. James Boncella and spent five years pursuing and sometimes clashing with organometallic and polymer chemistry. After completion of his Ph.D. in inorganic/organometallic chemistry, Jon will head off to Eastman Chemical Company to work as a postdoctoral scientist.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

James M Boncella

James M. Boncella, Chairman
Associate Professor of Chemistry

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May, 1999

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